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ERRATA

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Page 135:

In reference 12 substitute "Hintenberger" for "Hirstenberger."

In reference 20 substitute "Müller" for "Muller."

In references 27 and 28 substitute "Wittstadt" for "Willstadt."

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Page 320: The eight incomplete lines below the legend of figure 25 should be deleted.

Page 324: Figure 26 should appear as follows:

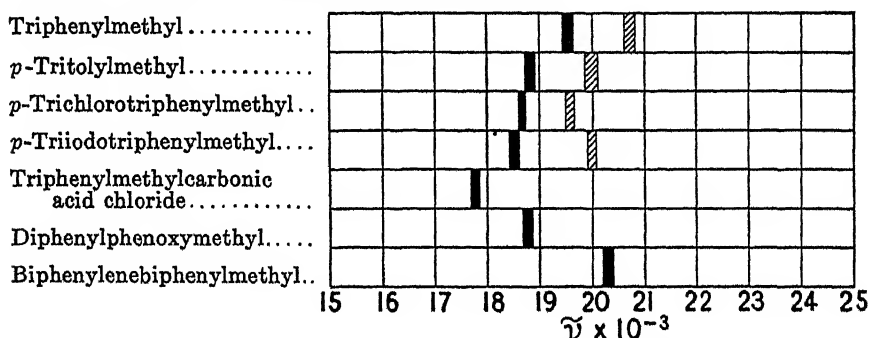


FIG. 26. Absorption spectra of the free radicals

THE CONSTITUTION OF COLLOIDAL SYSTEMS OF THE HYDROUS OXIDES¹

HARRY B. WEISER AND W. O. MILLIGAN

Department of Chemistry, The Rice Institute, Houston, Texas

Received November 14, 1938

I. INTRODUCTION

"Hydrous oxide" is the general term applied to the gelatinous precipitates thrown down from salt solutions above a critical pH value which varies for different salts. The term as we have used it for more than a quarter of a century implies that the gel water is held by the oxide by means of adsorption and capillary forces; hence the water content of a given hydrous oxide is the accidental result of the conditions of formation and drying and the age of the sample. The gels of ferric oxide, chromic oxide, titania, zirconia, and silica are typical hydrous oxides.

The elements of water are combined with certain oxides in definite stoichiometric ratios to give hydrated oxides or hydroxides, such as $\text{MgO} \cdot \text{H}_2\text{O}$ or $\text{Mg}(\text{OH})_2$, $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{Al}(\text{OH})_3$, $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or FeOOH , $\text{SnO} \cdot 0.5\text{H}_2\text{O}$, etc. Wherever the application of x-ray analytical methods discloses the presence of hydroxyl groups, it is customary to designate the preparation as a hydroxide rather than as a hydrated oxide, but the terms are used interchangeably. Gelatinous precipitates of such compounds are called hydrous hydrates or hydrous hydroxides.

On standing, the primary colloidal particles of hydrous oxides and hydroxides grow or coalesce and lose gel water spontaneously, causing the mass to assume a less gelatinous and more granular character. This aging or spontaneous transformation from a loose voluminous precipitate to a granular mass is accompanied by a decrease in the solubility, the adsorbability, and the peptizability of the compound.

The view that the hydrous oxide gels and sols consist of colloidal particles of oxide or of a simple hydrate with adsorbed and entrained water was defended by van Bemmelen (2) a half-century ago, but this rather elementary concept of the constitution of colloidal systems of the hydrous oxides is not accepted by certain investigators in this field. For example,

¹ Presented by Harry B. Weiser before the general meeting at the Ninety-fifth Meeting of the American Chemical Society, held in Dallas, Texas, April, 1938.

Willstätter, Krause, Kohlschütter, and Morley and Wood believe that the freshly precipitated oxide gels are best regarded as hydrates or orthohydroxides and that the aging process consists either of a polymerization or of a condensation involving the splitting off of water from one or more molecules of orthohydroxide to give polyhydroxides of gradually increasing complexity.

In the preface to a series of books on colloid chemistry the editor, Jerome Alexander, warns against any deceptive appearance of simplicity in nature and cautions, facetiously, that "It is we who are simple, not nature." Although no scientist would deny the complexity of most natural phenomena, it does not follow that the units of every system in nature must necessarily be of a complex character. At the risk of appearing old-fashioned and elementary minded, we shall present two types of experimental evidence that give strong support to the claim that most oxide gels and sols consist of agglomerates of minute crystals of oxide or simple hydrate (or hydroxide) rather than of polymerized bodies or condensation products of varying degrees of complexity. The evidence is derived from the simultaneous application of the time-honored phase rule technique and of the more recent x-ray diffraction analysis.

Experimental procedures

The application of the phase rule to the problem of the constitution of hydrous oxides has frequently led to erroneous conclusions in the past because of the nature of the systems and because of faulty technique. The temperature-composition curves at constant pressure (isobars) and the pressure-composition curves at constant temperature (isotherms) for hydrous oxide hydrates or hydroxides are, as a rule, not sharply defined step-curves. Moreover, the dehydration product may be highly hygroscopic, thereby modifying the form of the curve. Finally, in most instances the dehydration of the heavy metal oxides at constant pressure is reversible only over a very narrow range, and days or even weeks may be required to establish an equilibrium state at each temperature. If these characteristics of the systems under consideration are recognized, phase rule data may be obtained that are usually capable of definite interpretation.

In the laboratory of The Rice Institute, isobars are obtained by the simple expedient of heating the samples to constant weight at each temperature in a thermostatically controlled, hot-air oven through which is passed continuously air saturated with water vapor at 25°C. The isothermal dehydration is accomplished in an apparatus shown diagrammatically in figure 1. The general method of procedure consists in pumping off a definite amount of water and measuring the vapor pressure of the

resulting product at constant temperature by means of a manometer filled with "vacuum pump oil" of known density. The changes in composition are followed (1) by direct weighing of the sample tube with contents, (2) by collecting in a drying tube and weighing the water vapor pumped off at each pressure, or (3) by direct weighing of the sample with the

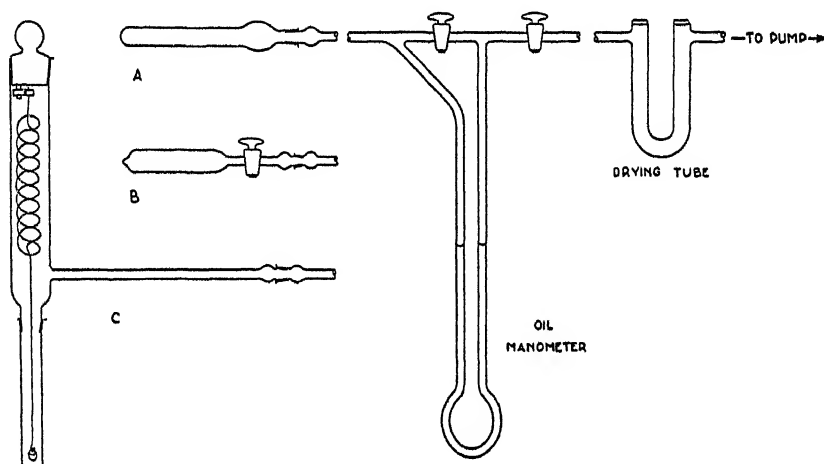


Fig. 1. Apparatus for isothermal dehydration

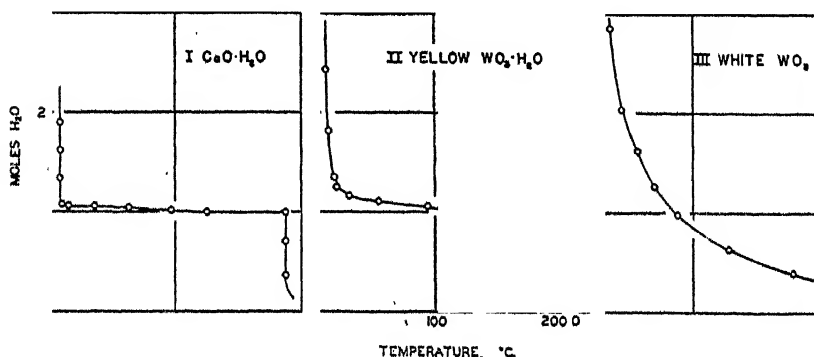


Fig. 2. Dehydration isobar for (1) hydrate or hydroxide, (2) hydrous hydrate, (3) hydrous oxide (after Hüttig).

McBain-Bakr balance (27). In figure 2 are given isobars which are typical of (a) macroscopic hydrates or hydroxides, (b) hydrous hydrates or hydroxides, and (c) hydrous oxides.

If the phase rule curve for a hydrous gel shows a definite point of inflection like that given in I of figure 2, there is no question but that the

elements of water are combined with the oxide in a definite stoichiometric ratio. In II the upper portion of the curve represents the loss of adsorbed or hydrous water by the hydrate; the middle portion corresponds chiefly to the loss of combined water; and the lower portion corresponds chiefly to the loss of water adsorbed by the anhydrous oxide. The rounded corners of the step are the result of the colloidal nature of the hydrous hydrate. In such colloidal precipitates there exists a wide variation in crystal size, and there is more or less crystal lattice distortion and crystal lattice strain. These facts, together with the marked tendency of both the hydrate and the dehydration product to adsorb water, account for the absence of sharp breaks in the dehydration curves of colloidal oxide hydrates. Hüttig (17) accounts for the form of the curve by assuming that only a part of the hydrate water is held definitely in place in the crystal lattice, whereas a part is "osmotically bound" or in solid solution and so may move about with more or less freedom. The evidence in support of Hüttig's point of view is not convincing. As a matter of fact, this type of curve is frequently obtained when the elements of water are present as $-OH$ groups rather than as H_2O molecules. Damerell (8, 9, 10) attributes the loss of water by a hydrate below a definite decomposition temperature to surface dehydration of extremely minute crystals without lattice rearrangement. This view is likewise reasonable, since one gets a similar form of curve even with macroscopic crystals. In any event, for certain hydrous hydrates the corners are rounded, and it is doubtful that the point of inflection corresponds to a definite chemical change or is absent altogether. Under these conditions examination of the dehydration product at intervals by the technique of x-ray diffraction may reflect greatly in establishing the constitution of the colloidal material. X-ray diffraction patterns are obtained by use with either a Seeman or a Phillips-McClure x-ray diffraction apparatus, using filtered $Ca K_\alpha$ x-radiation. The samples for examination are sealed in capillary tubes of Lindemann glass, which is quite transparent to x-rays.

In the following section the results of some observations on the constitution of typical hydrous oxide gels, obtained by using phase rule and x-ray diffraction technique, will be described; in the last section the results of the direct examination of hydrous oxide gels by x-ray diffraction analysis will be considered.

II. HYDROUS OXIDE GELS

A. Alumina

The well-defined hydrates of alumina exist in nature: $\gamma-Al_2O_3 \cdot 3H_2O$ (gibbsite) and $\alpha-Al_2O_3 \cdot H_2O$ (diaspore). Diaspore has not been prepared in the laboratory, but gibbsite is readily obtained by allowing alumina

gel thrown down from the salt solution with ammonia or alkali to age in the cold, especially in the presence of alkali, and by the slow hydrolysis of alkali aluminate. A sample of synthetic $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ was subjected to isobaric dehydration (58), waiting until equilibrium was established at each temperature. Samples heated for 2 hr. (insufficient for equilibrium to be set up) at various temperatures were examined by x-ray diffraction. The results are shown graphically in figure 3. It will be seen that $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ loses $2\text{H}_2\text{O}$ to give $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ as an intermediate product which, in turn, goes over to $\gamma\text{-Al}_2\text{O}_3$, and finally to $\alpha\text{-Al}_2\text{O}_3$ at elevated temperatures. This dehydration isobar is quite similar to that obtained by L. H. Milligan (32) for an artificial gibbsite and by Fricke and Severin (14) for a natural gibbsite. All the curves are alike in showing a rounded step corresponding

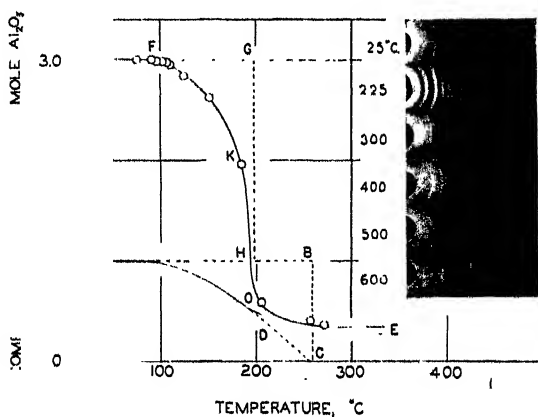


FIG. 3. Dehydration isobar and x-ray diffraction photographs of aluminas

to $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and in giving no indication whatsoever of the formation of a monohydrate as an intermediate product between $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and $\gamma\text{-Al}_2\text{O}_3$. But the x-ray evidence is indisputable that a colloiddally dispersed intermediate phase is obtained, which gives a distinctive diffraction pattern corresponding to $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (böhmite). The chemical individuality of this compound is evidenced by the fact that Fricke and Severin obtained macroscopic crystals of it by heating commercial $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ to 350–750°C. at a pressure of 200 atm. Hüttig and Peter (20) prepared a similar product by heating the trihydrate in a bomb tube at 200 atm. Particularly good crystals result on heating 4 to 20 per cent aluminum nitrate containing up to 20 per cent nitric acid at 320–360°C. and 200–300 atm.

Although the existence of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is established, this compound does not give a "step" dehydration isobar. Moreover, it was found

(58) that the x-ray diffraction pattern for $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ persists below a composition corresponding to $\text{Al}_2\text{O}_3 \cdot 0.35\text{H}_2\text{O}$. This anomalous behavior caused us at one time to doubt whether the intermediate product was a true hydrate; therefore it calls for special consideration.

Application of the phase rule to the two-component system mono-hydrate-oxide-water vapor shows that the system should be univariant, giving an isobar (58) represented by the dotted lines AB and BC in figure 3. Theoretically the curve should drop to zero composition at a definite temperature but, as we have pointed out, this never occurs with a colloiddally dispersed hydrate; instead, a part of the water is lost below the true decomposition temperature of the mass of the hydrate, and the curve takes the rounded form ADC . Now if the oxide formed by the dehydration of the hydrate is highly hygroscopic, it will adsorb most of the water vapor formed by the decomposition. Hence the actual dehydration measured is the loss of adsorbed water from the oxide. In such cases a bivariant type of curve is to be expected, as shown by the solid line AE in figure 3. It is this last type of curve that Fricke and Severin (14) obtained for both α - and $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

We may now explain the persistence of the x-radiogram for $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, where it would ordinarily not be expected. The x-radiogram of the monohydrate should persist along a part of the curve ADC because some of the compound is present, and the extremely hygroscopic $\gamma\text{-Al}_2\text{O}_3$ formed by partial decomposition of the monohydrate is either amorphous or too finely crystalline to be detected by x-ray analysis.

In a higher hydrate decomposing into a lower hydrate and finally into the anhydrous substance, it is apparent that, under the conditions noted above, the isobar alone will fail completely to detect the lower hydrate. The theoretical curves for a trihydrate decomposing into a monohydrate, and this in turn into the oxide, are given by the broken lines $F'GHBC$ in figure 3. Experimentally the composition of the trihydrate remains constant only to point F' , where some water is lost, giving a small amount of water vapor and monohydrate. As this process continues along the line FKH , all the trihydrate decomposes rapidly to monohydrate. Then the lower hydrate loses water to the point O ; hence the line FKH continues past the theoretical composition of the monohydrate to O . This decomposition of monohydrate gives the highly adsorptive $\gamma\text{-Al}_2\text{O}_3$, the presence of which causes the dehydration curve to follow the course HOE for the reasons given above.

Because of the extreme hygroscopicity of $\gamma\text{-Al}_2\text{O}_3$, the dehydration curve of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ shows such a marked variation from the theoretical curve that its existence as intermediate product in the dehydration of $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ has not been detected by phase rule technique. This is an extreme

case, but it is not unique. Adsorption of water by the dehydration product is responsible for the shape of the lower portion of the dehydration isobars of all colloidal oxide hydrates or hydroxides.

$\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or bayerite is a metastable compound isomeric with gibbsite, the stable modification. The dehydration isobar of bayerite is similar in essential respects to that of gibbsite.

The highly gelatinous precipitate thrown down at room temperature on adding ammonia to an aluminum salt solution gives the characteristic x-ray diffraction pattern of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. The patterns from the gel precipitated from nitrate and from chloride solutions are reproduced in figure 4, a and b. The series of alleged hydrates of alumina described by Prutton, Maron, and Unger (39) were prepared from aluminum chloride solution, and are probably $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ with varying amounts of adsorbed water.

Alumina gel free from other salts is best obtained by the action of amalgamated aluminum on water (68). Pure aluminum (99.6 per cent aluminum) is amalgamated in a mercuric chloride solution, washed thoroughly, and then placed in water. The gels prepared by its action for 24 hr. on boiling water and on cold water were examined by x-rays; the patterns are reproduced in figure 4, c and d. The gel thrown down in the hot gives the pattern of highly dispersed $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$; on the other hand, the gel obtained in the cold gives the typical patterns of $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or bayerite. Under the conditions described, the $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ first precipitated in the cold is transformed into $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. If sufficient time were allowed, this metastable compound would have gone to $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, gibbsite.

Failure in the past to recognize that $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ precipitated in the cold ages spontaneously in the cold, first to metastable $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ and finally to stable $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, has caused considerable confusion in interpreting the x-ray data of different investigators. It is now known, however, that samples of the metastable isomer are likely to contain more or less of the stable isomer, and that this apparently accounts for the differences in the bayerite patterns obtained by different people and for the presence in them of lines corresponding to $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. In a study of the transformation from alumina monohydrate to trihydrate by isobaric dehydration and x-ray diffraction methods, Hüttig was led to conclude that a continuous series of crystalline hydrates between the two extreme compositions was formed. It is very much more probable that the intermediate products are not definite chemical individuals as Hüttig (19, 21) suggests, but are mixtures of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$, and $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ in varying amounts, depending on the conditions of precipitation and the age and treatment of the samples.

In a study of the lake formation process ten years ago (51) it was observed that alumina gel (from amalgamated aluminum in the cold) lost its adsorption capacity for alizarin much more readily when prepared in the absence of chloride than when prepared in the presence of chloride. This was attributed, at the time, to the action of chloride in preventing the transformation of highly unsaturated atoms of aluminum on the surface of the gel into the normal lattice of crystalline alumina. We now know

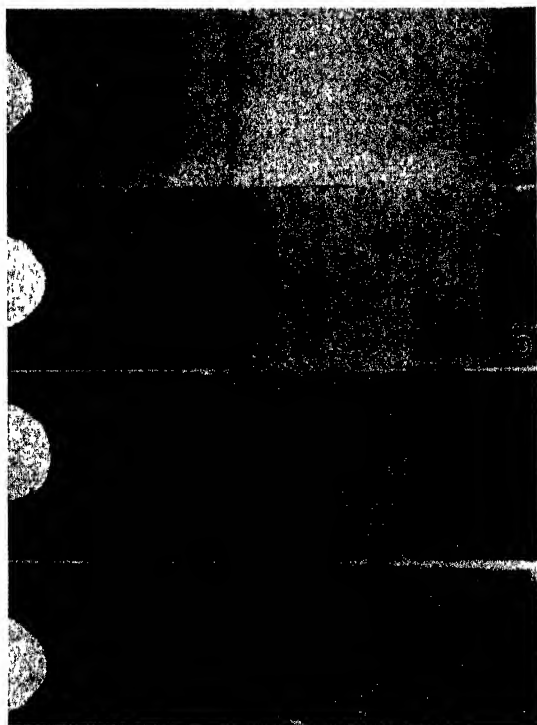


FIG. 4. X-ray diffraction photographs: $\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$ from (a) nitrate solution, (b) chloride solution, (c) amalgamated aluminum in the hot; and (d) $\alpha\text{-Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$ from amalgamated aluminum in the cold.

that the presence of chloride slowed down the following transformation: $\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O} \rightarrow \alpha\text{-Al}_2\text{O}_3\cdot 3\text{H}_2\text{O} \rightarrow \gamma\text{-Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$. In the absence of chloride this transformation of very highly dispersed $\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$ takes place fairly rapidly with the formation of larger crystals, chiefly of $\alpha\text{-Al}_2\text{O}_3\cdot 3\text{H}_2\text{O}$, having a relatively low adsorption capacity, whereas in the presence of chloride the highly colloidal $\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$ is more stable, and the gel retains its strong adsorption capacity for a longer period of time.

Willstätter and Kraut (64) describe several hydrous aluminas, differing

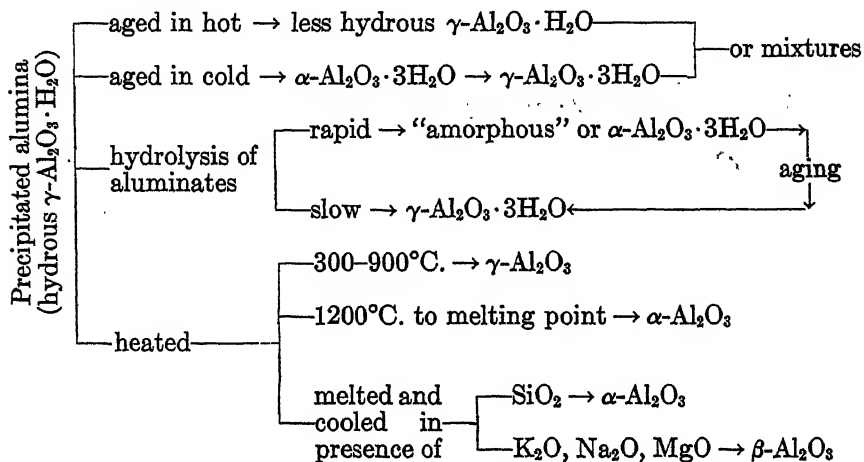
in reactivity and adsorptive power, prepared by precipitating aluminum sulfate with ammonia under varying conditions. A suspended precipitate into which steam was conducted for 5 hr. was a pale yellow plastic mass, *A*; without the steam treatment, it was a very pale yellow plastic mass, *B*; precipitated with more dilute ammonia it was a pure white, very voluminous, and very finely divided substance, *C*. An intermediate variety, *D*, prepared by the dialysis of aluminum chloride with frequent additions of small quantities of ammonia, was claimed to be related chemically to *B* but resembled *A* in adsorptive power; a modified form of *C*, precipitated at 60°C., had an adsorptive capacity similar to that of *B*; and a new (67) form of *A*, claimed to be $\text{Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$, was obtained by carrying out the precipitation at approximately 50°C., washing by decantation four times, followed by the addition of 15 per cent ammonia, and further washing by decantation until peptization started. As a result of dehydration experiments with the gels, Willstätter claimed that he obtained various hydrates which gave certain temperature intervals of almost constant water content. Thus precipitates obtained at low hydroxide-ion concentration and washed with acetone, which was tacitly assumed to remove adsorbed water, analyzed approximately for trihydrate; and precipitates obtained with excess ammonia in the hot gave what were assumed to be polyaluminum hydroxides, such as $2\text{Al}(\text{OH})_3 \cdot \text{H}_2\text{O}$, $4\text{Al}(\text{OH})_3 \cdot 3\text{H}_2\text{O}$, and so on up to $8\text{Al}(\text{OH})_3 \cdot 7\text{H}_2\text{O}$. X-ray analysis of the several preparations (3, 54) showed that most of Willstätter's alleged hydrates have no existence in fact. Thus the preparations of *B* and new *A* all gave the x-ray pattern of the monohydrate $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$. This is sharp from the pattern of the gels from the chloride and nitrate (Figure 11). If the preparations originally $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ are aged under suitable conditions, and in the lines corresponding to $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\gamma\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ has appeared in the x-ray diagram. But Willstätter's gels are all the same essentially $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ which differ in particle size and in degree of crystallinity, hence they show marked differences in their behavior toward dyes and in their adsorption capacity for dyes and enzymes.

Thiessen (55) has prepared the electrolytic treatment of aluminum sulfate. The initial highly hydrous gel has a present composition corresponding to the aged, more granular gel of the point of maximum in the pressure-composition curve for $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The new gel is probably hydrous $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$. The aged gel gave the x-ray pattern of $\alpha\text{-Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$.

Finally, Willstätter has prepared a new form of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ by aging a gel of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ in a solution of H_2SO_4 and then washing with water. The new form is $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ and is identical with the original $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

pending on the conditions of preparation. The crystal structure of none of these compounds is known with certainty, but α - $\text{Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (diaspore) and γ - $\text{Al}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ (gibbsite) have been investigated recently by Ewing (12) and Megaw (31).

The various transformations of precipitated alumina are shown in the following diagram:



B. Gallia

Gallia, like alumina, forms a definitely crystalline trihydrate (24a)² and a hydrous monohydrate under suitable conditions. The gel, freshly precipitated at room temperature by the addition of alkali to a gallium salt, is hydrous Ga_2O_3 . On standing in contact with ammonium hydroxide or on reprecipitation from a solution in ammonium hydroxide, hydrous Ga_2O_3 is transformed into hydrous $\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which gives a dehydration isobar with a point of inflection corresponding to a monohydrate and a distinct x-ray diffraction pattern.

The gel thrown down at 100°C. consists of larger particles of hydrous Ga_2O_3 than are formed in the cold. Because of the lower solubility of the larger particles the gel does not age to monohydrate as readily as the oxide precipitated at room temperature. The dehydration isobar of the 100°C.-gel is continuous, and the x-ray diffraction pattern consists of two or three broad bands. Samples heated to higher temperatures show a progressive decrease in the width of the most prominent diffraction bands and the appearance of additional bands, indicating that the hydrous oxide is recrystallizing to form larger primary particles as the temperature is increased.

The results of observations (34) on precipitated gallia are summarized in figure 5. It is apparent that the upper curve exhibits a point of inflec-

² Added to proof.

tion corresponding to a monohydrate, although this might very well be overlooked if it were not for the simultaneous x-ray diffraction data. The diffraction pattern for $\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$ (5) is entirely different from that of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

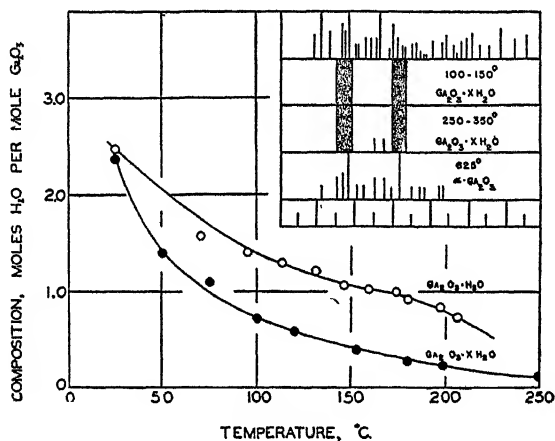


FIG. 5. Dehydration isobars and x-ray diffraction patterns of gallias

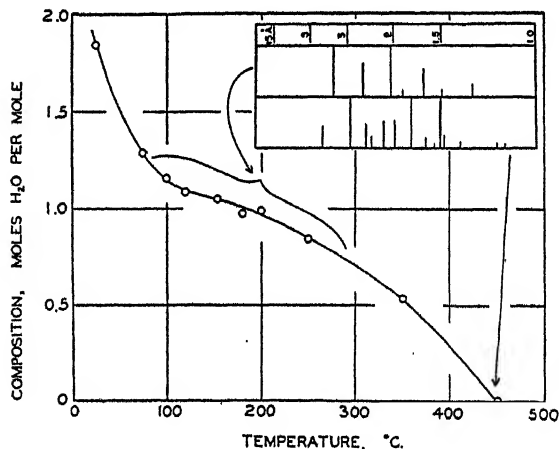


FIG. 6. Dehydration isobar and x-ray diffraction patterns for hydrous scandium oxide monohydrate

C. Scandia

Scandia gel precipitated either at room temperature or at 100°C . is a highly gelatinous mass which gives a definite dehydration isobar corresponding to hydrous $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Figure 6 (63) gives the dehydration and x-ray data for a gel thrown down at 25°C . The alleged compound of

Štěrbá-Böhm and Melichar (41), $[2\text{Sc}(\text{OH})_3] \cdot \text{H}_2\text{O}$, gives the same diffraction pattern as the precipitated gel, $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$.

For purposes of comparison, the diffraction patterns of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$, and $\text{Ga}_2\text{O}_3 \cdot \text{H}_2\text{O}$ are shown together in figure 7. The close resemblance between the pattern of $\text{Sc}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which gives a monohydrate dehydration isobar, and that of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, which does not give a monohydrate isobar, indicates a similarity in both constitution and crystal structure.

D. The hydrous oxides of tin

Hydrous stannic oxide. As early as 1812 Berzelius called attention to differences between the hydrous oxide formed by precipitation of stannic chloride with alkali and the product resulting from the action of nitric acid on tin. Since both preparations give a very slight acid reaction when shaken with water, they are commonly designated as orthostannic and

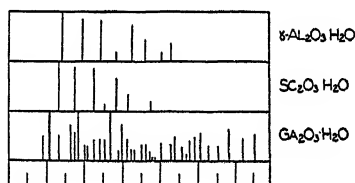


FIG. 7. Diagrams of the x-ray diffraction patterns for the hydrous monohydrates of the oxides of aluminum, scandium, and gallium.

metastannic acid, respectively. Earlier chemists regarded them as distinct chemical individuals with sharply defined differences.

Early investigators reported the preparation of a variety of supposedly definite oxide hydrates and hydrated acids of tin, obtained by drying the different preparations under suitable conditions, but extended investigations of van Bemmelen (2), Lorenz (26), Mecklenburg (30), and Weiser (50) failed to establish the existence of any preparation in which the elements of water are combined in a definite stoichiometric ratio. In recent years, however, Willstätter (65, 66) and his collaborators have adopted the older view that the behavior of different oxides could best be explained by assuming the existence of more or less stable hydrates. Willstätter claimed that all adsorbed water was removed from a gel by drying rapidly in a vacuum or by leaching with acetone. The composition of a gel formed in a special way and dried by the acetone method at -35° to $+10^\circ\text{C}$. was represented by the formula $\text{Sn}(\text{OH})_4 \cdot 4\text{H}_2\text{O}$; when the gel was dried at room temperature it analyzed for $\text{Sn}(\text{OH})_4$, which was regarded as the first member of a series of ortho- or α -stannic acids. In an aqueous medium

$\text{Sn}(\text{OH})_4$ was supposed to go over into other less basic members of the series. Thus by suitable conditions of precipitation and drying with acetone at 0° to 10°C ., orthodistannic acid was supposedly formed; at 35° to 46°C . orthotristannic acid; and so on. Different so-called metastannic acids were likewise prepared and formulas assigned to many of them.

As evidence of hydrate formation Willstätter cites the regions of almost constant water content in the temperature-composition curves of acetone-dried preparations. Such evidence is altogether inconclusive, particularly in view of the fact that the nature and location of the "flats" in the curves are determined almost exclusively by the history of the sample. Such behavior was noted by van Bemmelen almost forty years before Willstätter. The adsorptive capacity of a true hydrous oxide for water at different stages of dehydration is determined by the physical character of the preparation; hence a "flat" corresponding to a hydrate is purely accidental and can be duplicated only by following a set method of procedure in precipitating, aging, and drying. Willstätter's comparison of the behavior of hypothetical, high molecular, hydrated stannic acids with their groups $\text{Sn}:\text{O}$ and $\text{Sn}\cdot\text{OH}$ to that of carbohydrates with their groups $\text{C}:\text{O}$ and $\text{C}\cdot\text{OH}$ appears to us highly fantastic and illusionary. As Posnjak (37) pointed out in 1926: "Willstätter and his collaborators did not bring forth a single new fact, but rather take the problem back some fifty years and only add to the confusion."

In support of his criticism of Willstätter's point of view Posnjak showed that samples of the so-called ortho- and meta-stannic acids give identical x-ray diffraction patterns, which in turn are identical with that of the mineral cassiterite, anhydrous SnO_2 . This result has been confirmed by Yamada (70), Förster (13, 16), Hüttig and Döbling (18), and others, so that there is no question about the facts. The ortho- and meta-acids (α - and β -oxides) are not isomers but are structurally identical stannic oxide with more or less adsorbed water. The differences in properties cannot be traced to differences in composition or crystal structure, but are due to differences in size and extent of coalescence of primary crystalline particles into secondary aggregates.

Although precipitated stannic oxide, as ordinarily prepared, is always hydrous SnO_2 and forms no hydrates or hydroxides, simple, condensed, or polymerized, Thiessen and Körner (43) claim that a stannic oxide gel prepared by the slow hydrolysis of an alcoholic solution of stannic ethylate gives isobars and isotherms that indicate the formation of no less than six definite hydrates. This could not be confirmed by us (55), as is shown by the dehydration isobar given in figure 8, together with similar isobars for typical α - and β -oxides. In every instance smooth curves were obtained, indicating the absence of hydrates. The change in direction of the

curve for a Thiessen-Körner preparation at 60–70°C. is due not to hydrate formation but to the presence of some adsorbed alcohol on the sample. The breaks in the curves of Thiessen and Körner may result from faulty technique, possibly from the failure to allow sufficient time for equilibrium to be established under a given set of conditions. Finally, x-ray diffraction examination of gels obtained by dehydrating a Thiessen-Körner preparation to temperatures corresponding to alleged hydrates, all give a band pattern corresponding to cassiterite, indicating that the several alleged hydrates consist of stannic oxide of varying degrees of agglomeration and with varying amounts of adsorbed water.

Thiessen claims that his hydrates are metastable bodies which have to be caught "on the run," and that we missed them by attempting to get

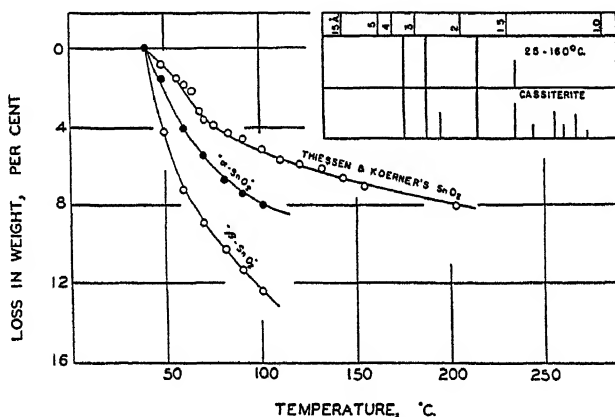


FIG. 8. Dehydration isobars and x-ray diffraction patterns for hydrous stannic oxide

points on the curve corresponding to equilibrium conditions. It is a brave man who trusts phase rule data obtained under non-equilibrium conditions. Moreover, it is not obvious why metastable hydrates should give the x-ray diffraction pattern for the anhydrous oxide, unless one wants to assume that the samples examined were mixtures of a hydrate amorphous to x-rays and the anhydrous oxide, and that only the pattern of the latter showed up. If this assumption were true, the "steps" would not come at exact stoichiometric ratios as found by Thiessen and coworkers, but at a lower ratio of H_2O to oxide, which would be determined by the relative amounts of the "amorphous hydrate" and crystalline anhydrous oxide present.

Hydrous stannous oxide. The precipitate obtained by the interaction of stannous salts and an alkali is usually erroneously formulated as $\text{Sn}(\text{OH})_2$. Bury and Partington (7) claim that the precipitate dried in vacuum over phosphorus pentoxide has the composition $3\text{SnO} \cdot 2\text{H}_2\text{O}$.

Actually, the gel is hydrous $\text{SnO} \cdot 0.5\text{H}_2\text{O}$, as evidenced by the phase rule and x-ray data shown graphically in figure 9 (56). The white or faintly yellow gel thrown down from stannous chloride solution with ammonia was washed practically free from chloride, first by the centrifuge until peptization started and then with a supercentrifuge. Air-dried samples were subjected to isobaric dehydration in a current of nitrogen and examined by x-rays at intervals. The results show conclusively that the preparation is a hydrous hemihydrate which starts to decompose at a temperature of 120°C . to give $\alpha\text{-SnO}$. Comparable to the behavior of copper hydroxide, the gel of $\text{SnO} \cdot 0.5\text{H}_2\text{O}$ dehydrates spontaneously to $\alpha\text{-SnO}$ at room temperature in the presence of excess alkali. It is also dehydrated by the action of light, especially in the absence of free ammonia.

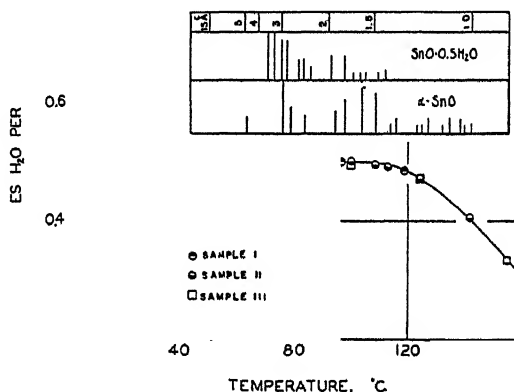


FIG. 9. Dehydration isobar and x-ray diffraction patterns of stannous oxides

E. Titania

The hydrous oxides of TiO_2 , ZrO_2 , and ThO_2 are always described as existing in both an alpha-(or ortho-) and a beta-(or meta-)modification. Actually, in every case the relationship between the two alleged isomers is the same as exists between the so-called alpha- and beta-stannic oxides.

The product commonly referred to as orthotitanic acid is a white gelatinous precipitate thrown down by the addition of ammonia or alkali hydroxide to a solution of tetravalent titanium salt. Metatitanic acid is a granular, difficultly soluble preparation obtained (1) by aging the orthotitanic acid, (2) by the action of nitric acid on titanium, or (3) by hydrolysis of boiling solutions of titanium chloride. These alleged acids or oxide hydrates do not exist; both are hydrous oxides, as evidenced by the form of the dehydration isobars (57) shown in figure 10. Here again, the difference between the two preparations in solubility, adsorbability, and

peptizability is a question of specific surface and not of isomerism. Aging involves not the condensation or polymerization of orthohydroxides, but the growth, coalescence, and agglomeration of primary particles into coarser aggregates.

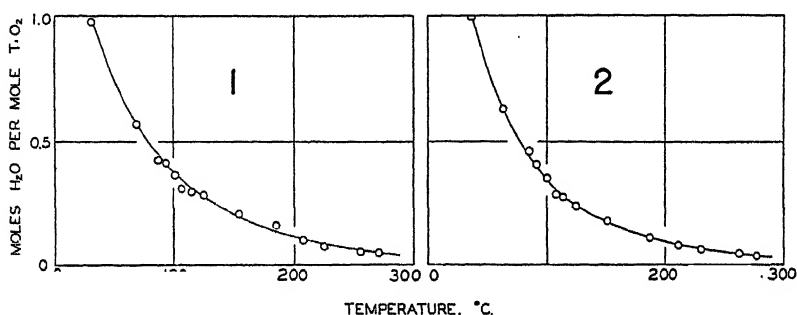


FIG. 10. Dehydration isobars for hydrous titanium dioxide: 1, precipitated at room temperature; 2, oxidation of $\text{Ti}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ in air.



PRECIPITATED AT ROOM TEMPERATURE
 $\text{Ti}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ OXIDIZED IN THE AIR

No. 1 AGED 30 WEEKS AT ROOM TEMP.

No. 1 HEATED TO 184°

No. 1 AGED 6 HOURS AT 100°

PRECIPITATED AT 100°

HYDROLYSIS OF $\text{Ti}(\text{SO}_4)_2$

MINERAL ANATASE, TiO_2

HYDROLYSIS OF TiCl_4 OR $\text{Ti}(\text{NO}_3)_4$

MINERAL RUTILE, TiO_2

No. 1 HEATED TO 1000°

No. 2 HEATED TO 1000°



FIG. 11. Diagrams of the x-ray diffraction patterns of titanias

A summary of the x-ray diffraction data (57) obtained with titanias prepared and treated in different ways is given in figure 11. It is an interesting fact that the gel formed by hydrolysis of titanium chloride or nitrate gives an x-radiogram corresponding to the rutile modification of

titania, whereas hydrolysis of titanium sulfate under similar conditions gives the anatase modification of the oxide. The gel precipitated from titanium chloride or nitrate solutions at 100°C. with ammonia gives a pattern corresponding to anatase. This behavior may well be of primary importance in connection with the manufacture of titania pigments.

The aging of the freshly precipitated oxide is a continuous process, which can be followed by observing (1) the sharpening of the anatase lines in the x-ray diffraction pattern, (2) the decrease in the adsorption capacity for dyes, and (3) the falling off in the solubility and peptizability in hydrochloric acid. In the light of the phase rule and x-ray studies, there seems no experimental justification for assuming, as Morley and Wood (35) do, that the change in physical character of the gelatinous oxide on aging is due to the formation of complex salt-like condensation products by the molecules of alleged hydroxides functioning both as acid and as base.

F. Hydrous ferric oxide

The brown gel. The brown gel of hydrous ferric oxide, frequently misnamed ferric hydroxide, is commonly prepared by the addition of a base to a solution of ferric salt. Since a small integral ratio between oxide and water may be realized by drying the gel under suitable conditions, hydrates of the oxide have been reported from time to time, but most of the experimental evidence indicates that the brown precipitate gives no hydrates on isobaric or isothermal dehydration. The isobars (40) of two gels thrown down at room temperature are typical desorption curves showing no indication of the presence of $\text{Fe}(\text{OH})_3$ or any other hydrate (figure 12). Curve 1 is for a relatively coarse sample formed by precipitation of a ferric nitrate solution with ammonia, and curve 2 is for a finer grained sample thrown down from a ferric chloride solution with ammonia. The gel freshly formed in the cold is amorphous to x-rays, but after standing at room temperature in contact with water for several weeks it gives a band diffraction pattern corresponding to $\alpha\text{-Fe}_2\text{O}_3$ or hematite (59), and after several months the aging has progressed to the point where the sample gives a sharp hematite pattern. The aging of the brown gel consists in the growth of $\alpha\text{-Fe}_2\text{O}_3$ crystals too small to give a characteristic x-radiogram into crystals large enough to give sharp diffraction lines. This transformation takes place slowly at room temperature but more rapidly at high temperature. The gel thrown down at 100°C. gives at once a band pattern of $\alpha\text{-Fe}_2\text{O}_3$; if maintained for a few hours at this temperature, it gives a sharp line pattern. A gel precipitated at 50°C. and held at this temperature for a few hours gives broad diffraction bands corresponding to $\alpha\text{-Fe}_2\text{O}_3$. It would appear, therefore, that the brown gel precipitated at room temperature is hydrous $\alpha\text{-Fe}_2\text{O}_3$.

The only physical evidence of the formation of hydrate or hydroxide by dehydration of the brown gel was furnished by the phase rule studies of Thiessen and Köppen (42) on a gel thrown down by the slow hydrolysis of ferric ethylate. During the isothermal dehydration of this gel, Thiessen and Köppen reported breaks corresponding to no less than eight and

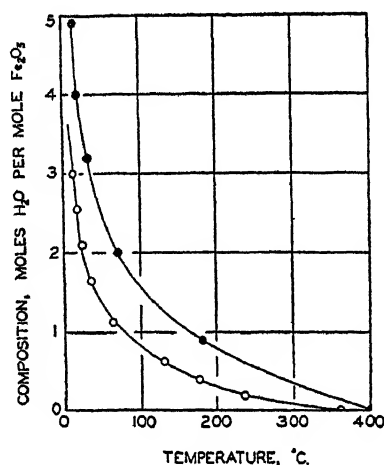


FIG. 12. Dehydration isobars for hydrous ferric oxides

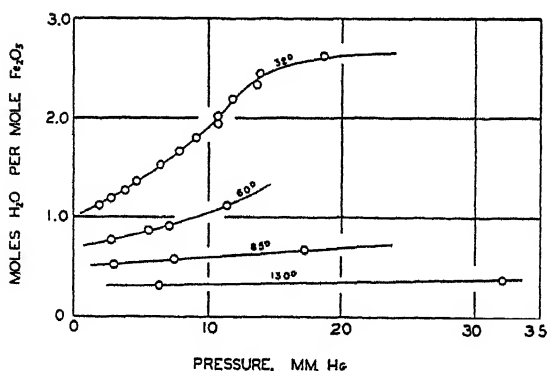


FIG. 13. Dehydration isotherms for $\text{Fe}_2\text{O}_3 \cdot x\text{H}_2\text{O}$ prepared by Thiessen's method

possibly ten different hydrates: $\text{Fe}_2\text{O}_3 \cdot n\text{H}_2\text{O}$, where $n = 5.0, 4.5, 4.0, 3.5, 3.0, 2.5, 2.0, 1.5, 1.0$, and 0.5 . We have repeated these experiments and failed to find any indication of a break corresponding to any one of the remarkable series of "Thiessen hydrates." A typical set of isotherms is reproduced in figure 13 (59). Thiessen questioned the purity of our preparations, and so the experiments were repeated with a gel formed by

slow hydrolysis at 15°C. of a specially prepared sample of ferric ethylate. Again, smooth dehydration isotherms were obtained. The only real difference between our experimental procedure and that of Thiessen is that we allowed time for equilibrium to be substantially established at each pressure, whereas Thiessen waited for a length of time which he knew was insufficient for equilibrium to be set up. Thiessen justified his unusual procedure in phase rule work because of the supposed transient nature of the alleged hydrates. In our observations of the rate at which equilibrium is established we failed to detect any indication of such metastable hydrates.

Krause (24) and his collaborators claim the existence of ortho- and meta-hydroxides of iron, as well as a variety of products of aging, on the basis of the results of procedures involving the synthesis of silver ferrites. Krause assigns definite molecular structures to the freshly formed gels and interprets the changes on aging to polymerization, ring closure, aggregation, oxygen bridging, etc. This view ignores the results of x-ray diffraction and phase rule work. At best it is of limited application, since even the highly hydrous 100°C.-gel is $\alpha\text{-Fe}_2\text{O}_3$ with adsorbed and capillary-bound water. Willstätter and coworkers (64, 66) likewise claim that the water in the brown gel is held in part as chemically combined water and in part as capillary-bound water. They claim to be able to remove the capillary water by washing with acetone, leaving definite hydrates the composition of which depends on the conditions of drying. As we have seen, these claims are not justified by Willstätter's experiments and are not taken seriously by most people.

Hydrous ferric oxide monohydrates. Two monohydrates of ferric oxide exist in nature: $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$, or göthite, and $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$, or lepidocrocite. These give characteristic x-ray diffraction patterns and step dehydration isobars, $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ yielding $\alpha\text{-Fe}_2\text{O}_3$ and $\gamma\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ yielding $\gamma\text{-Fe}_2\text{O}_3$.

The α -monohydrate may be synthesized (1) by oxidation of ferrous salts under suitable conditions, (2) by aging the brown gel in 2 *M* potassium hydroxide at 150°C., and (3) by slow hydrolysis of most ferric salts. The last procedure is probably the simplest. In 1920 it was observed (49) that a solution of ferric acetate which had stood for a week or two at room temperature gave a yellow precipitate on prolonged boiling to remove the excess acetic acid followed by coagulating the resulting sol. From a freshly formed acetate solution treated in the same way, a red coagulum was obtained. It was believed at the time that both the yellow and red preparations were hydrous ferric oxides which differed from each other in physical structure, but it is now known from x-ray analysis that the yellow coagulum was hydrous $\alpha\text{-Fe}_2\text{O}_3\cdot\text{H}_2\text{O}$ and the red was hydrous $\alpha\text{-Fe}_2\text{O}_3$. Posnjak and Merwin (38) obtained the same compound from

dilute solutions of ferric sulfate; more concentrated solutions yielded a basic salt. The results of observations with a number of ferric salts are summarized in table 1 (59).

The γ -modification of $\text{Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ is synthesized preferably by the oxidation of ferrous iron compounds under conditions that favor the formation of an intermediate iron complex (1).

TABLE 1
Slow hydrolysis of ferric salts

| SALT HYDROLYZED | PRODUCT IDENTIFIED BY X-RAY ANALYSIS |
|---|--|
| Sulfate..... | $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3 \cdot 9\text{H}_2\text{O}$ |
| Nitrate..... | $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ |
| Nitrate (with trace of $\beta\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$).... | $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ |
| Bromide..... | $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ |
| Oxalate..... | $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ |
| Acetate..... | $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ |
| Chloride..... | $\beta\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$ |

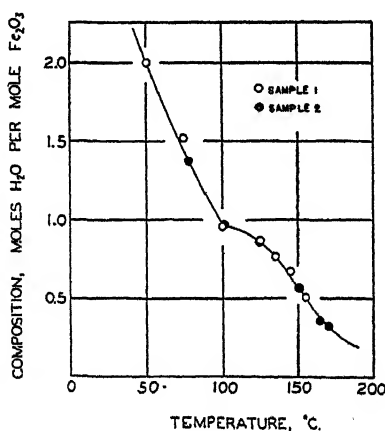


FIG. 14. Dehydration isobar for $\beta\text{-FeOOH}$

In table 1 it will be noted that when aqueous solutions of ferric chloride are allowed to stand at room temperature or are heated slowly to 60–100°C., a yellow hydrous precipitate is deposited which is not $\alpha\text{-Fe}_2\text{O}_3 \cdot \text{H}_2\text{O}$. Since the precipitate contains chloride and gives a distinctive x-radiogram, it is frequently regarded as a basic salt. We have found, however, that practically all the chloride may be removed without modifying the x-radiogram. Moreover, the dehydration isobar corresponds to that of a hydrous monohydrate. The results (60) of isobaric dehydration examination are summarized in figure 14.

The yellow precipitate from ferric chloride has been named β -ferric oxide monohydrate to distinguish it from the α - and γ -monohydrates. Kolthoff (23) believes that the compound should be formulated β -FeO(OH) and that the chloride it carries down with it is isomorphous FeOCl in solid solution. Kolthoff may be right, but his experimental evidence is insufficient to justify his conclusions.

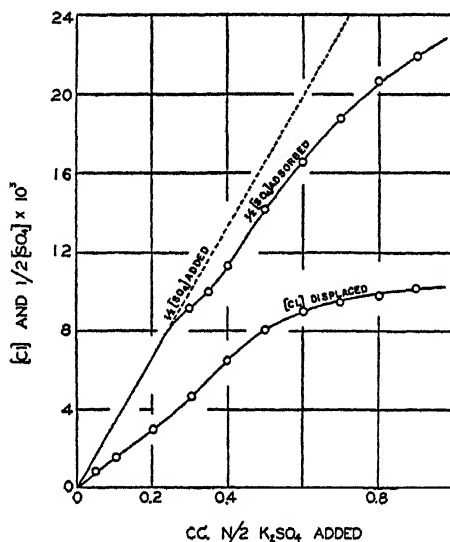


FIG. 15. Simultaneous displacement of chloride and adsorption of sulfate on titrating alumina sol with potassium sulfate

III. HYDROUS OXIDE SOLS

Sols of the hydrophobic type, which includes most of the hydrous oxides, can be prepared fairly free from electrolytes, but it was demonstrated first by Thomas Graham and confirmed repeatedly thereafter that, in the absence of protecting colloids, some electrolyte must be present in the sols to ensure their stability. Thus ferric oxide sol formed by hydrolysis of ferric chloride or by peptization of the hydrous oxide gel with ferric chloride always contain more or less chloride. Solum sols containing no detectable chloride either contain a trace of some other electrolyte or are protected by some material derived from the dialyzing membrane during the prolonged dialysis.

The presence of chloride in the dialyzed sols led Wyruboff and Verneuil (69) to suggest that the various preparations contain basic salts or chlorides of condensed hydroxides. This idea was further extended and developed by Duclaux (11), Malfitano (28, 29), Hantzsch and Desch (15), and Linder

Larger complexes are assumed to result from dissociation of any of the water molecules in nuclei like the above and olation among such nuclei through the hydroxo groups thus formed. The existence of such complexes was assumed to account, among other things, for the observation that the pH value of the sol is raised by the stepwise addition of neutral salts, the anion order being oxalate > acetate > sulfate > halides > nitrate. The increase in pH value was attributed to replacement of OH groups by the anion of the added salt, followed by the union of the displaced OH radicals with hydrogen ion to form water.

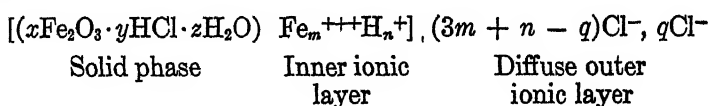
Now we have seen that the gel formed by the action of amalgamated aluminum on water at 100°C. is $\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$, and we shall see that the dispersed phase in a sol prepared by Thomas' procedure is $\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$. As already pointed out, we do not know the exact crystal structure of $\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$, but it is probably similar to that of diasporite, $\alpha\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$, which has been represented as $\text{AlO}(\text{OH})$ (12). In any event, when the crystal structure of $\gamma\text{-Al}_2\text{O}_3\cdot\text{H}_2\text{O}$ is known, the structure of the dispersed phase in Thomas' alumina sol will be the same.

Since hydrous oxide sols formed in the presence of chloride, say, always contain more or less chloride, Thomas believes that such sols should be designated as metallic oxychloride sols rather than as hydrous oxide sols. He recognizes that the term "ferric oxychloride hydrosol" is objectionable, since it connotes a definite chemical compound when no such meaning is intended. Nevertheless, he prefers to refer to hydrous oxide sols as oxysalt sols, since the colloidal particles are not pure hydrous oxides or hydroxides. To be consistent, the metal sols and salt sols should be renamed, since the dispersed phase is not pure metal and salt, respectively. It is difficult to see what would be gained by introducing such a change in our terminology. The ratio of iron to chlorine in a ferric oxide sol has been variously reported as 6, 42, 84, 396, 2700, and higher. To designate a sol with a low chloride content as an oxychloride sol is like calling precipitated barium sulfate a chlorosulfate because it contains some adsorbed barium chloride.

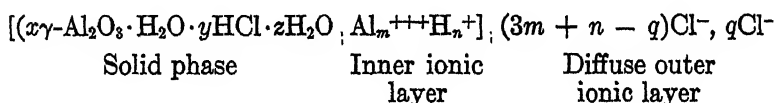
It is now quite generally recognized that the stability of a positive silver halide sol results from preferential adsorption of silver ions by unsaturated secondary valence forces on the surface of the crystals. The crystals may also contain some adsorbed silver nitrate. Similarly, a hydrous oxide sol formed in the presence of metallic chloride, hydrochloric acid, and their corresponding ions will contain varying amounts of the several components, depending on the precise method of formation and purification of the sol. The positive charge on a given sol is due to the preferential adsorption of metallic ion and hydrogen ion, just as the positive charge on a positive silver halide sol is due to preferential adsorption of silver ion. It is unnecessary to attribute the charge to the presence of an "ionogenic complex attached to the surface" (Pauli), unless the presence of such a

complex is known or rendered highly probable. Thus, to assume the presence of a simple salt like FeOCl on the surface of the particles of a ferric oxide sol goes well beyond the established facts.

In recent years investigations have been made of the various phenomena that accompany the stepwise addition of coagulating electrolytes to sols (52, 53, 62). For example, the addition of sulfate to a sol of hydrous alumina results in adsorption of sulfate and displacement of chloride from a diffuse ionic layer surrounding the particles. Figure 15 is typical of such adsorption and displacement curves. To account for the observed facts, the constitutions of two typical hydrous oxide sols are represented as follows:



and



This formulation of the constitution of certain oxide sols is accepted by Iyer (22), but he suggests that the diffuse portion of the double layer contains displaceable hydroxide ions as well as chloride ions. The displacement of hydroxide ions by the anions of neutral salts would account for the increase in pH value emphasized by Thomas, but it seems questionable whether hydroxide ions will be present in the outer portion of the ionic double layer in sols having a pH value of 4 to 5. We have attributed the increase in pH value of alumina sol on adding neutral salts, especially those with multivalent anions, to increase in adsorption of hydrogen ion in the presence of a strongly adsorbed anion. This increase in the adsorption of cations in the presence of strongly adsorbed anions is a general phenomenon that has been observed repeatedly with various types of adsorbents, such as carbon and fibers, as well as the hydrous oxides. It may be that a part of the increase in pH value on adding neutral salts to alumina sol is due to the replacement of OH groups from $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ by the added ion, but the existence of such an interchange is still questionable. If this happens, it means that anions such as $\text{C}_2\text{H}_3\text{O}_2^-$, Cl^- , and SO_4^{--} displace OH groups from the crystals of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ or $\gamma\text{-AlO} \cdot \text{OH}$. The experiment should be tried with crystals of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$ above the colloidal range in size where adsorption phenomena, which will produce a similar effect on the pH value, take place to a relatively small extent. It must be kept in mind that with salts such as citrate, oxalate, and acetate

buffer action will tend to increase the pH value of the sol-electrolyte mixtures above that of the sol alone.

From the evidence obtained by titration of oxide sols with neutral salts there is no necessary reason for assuming that the sols are colloidal electrolytes consisting of basic salts or Werner complexes. On the contrary, the indirect evidence suggests that the dispersed phase consists essentially of hydrous oxide (or simple hydrate or hydroxide).

Since x-ray diffraction analysis has proven helpful in determining the constitution of gels, one would expect this technique to be useful with sols. Until recently, however, the application of x-ray diffraction methods to sols has been indirect; the sols have been coagulated or ultrafiltered and the resulting gel, either dry or moist, has been examined. For example, we found (61) that the moist gels obtained by ultrafiltration of alumina, stannic oxide, and indium hydroxide sols gave the patterns of $\gamma\text{-Al}_2\text{O}_3 \cdot \text{H}_2\text{O}$, SnO_2 , and $\text{In}_2\text{O}_3 \cdot 3\text{H}_2\text{O}$ or $\text{In}(\text{OH})_3$, respectively. Although it is often assumed that the sol particles have the same constitution in the sol state as in the gel from the sol, only the direct examination of the sols by x-ray diffraction methods can decide whether this is the case.

Björnsthål (4) first examined gold and silver sols directly by allowing them to flow through a tube of gold-beater's skin centered in the x-ray camera and obtained patterns like those for metallic gold and silver respectively. The important investigations of Böhm and Niclassen (6) on the gels of various hydrous and hydrated oxides and hydroxides have been supposed by some people to include studies on sols in the sol state, but in a private communication Böhm writes: „Die Aufnahmen für die Arbeit in der Z. f. anorganische Chemie, 132, 1 (1924) wurden, wie Sie richtig vermuten, an den meist fruchten *Rückständen* von Solen nach dem Koagulation oder Eindampfen (so beim Crum'schen Sol) gemacht.“ In the same communication Böhm states that he and Ganter examined *liquid sols* of aged ferric oxide and vanadium pentoxide by allowing them to flow through a Mark tube and observed some indication of orientation of the needle-like particles.

In 1934 we examined directly a Péan de St. Gilles ferric oxide sol which we sealed in a Nonex glass tube and exposed to x-rays for 96 hr. in a General Electric apparatus. The resulting diffraction pattern was the same as that for $\alpha\text{-Fe}_2\text{O}_3$. The experiment was not altogether convincing, since such long exposure to x-rays may have caused partial coagulation of the sol.

The chief difficulties in the direct examination of sols by x-rays are as follows: (a) the relatively low concentration of the solid phase, (b) the scattering of the x-rays by the water in the sample, and (c) the possibility of coagulation of the sol by x-rays. The first and second difficulties were

obviated by using fairly concentrated sols and the third by flowing the sols continuously through the camera (33). Some objections may be made to flowing the sol through a tube of any kind; hence the sols were allowed to flow in an unenclosed column in the same way that Debye originally examined liquids. A Debye-Scherrer type of camera was employed, a diagram of which is shown in figure 16. Cu K_{α} x-radiation from a Philips cross-focus tube was used. The exposure time was 30-60 min. To identify the patterns from the several sols, x-radiograms (33) were made from the corresponding powders. The results obtained from pure water, the

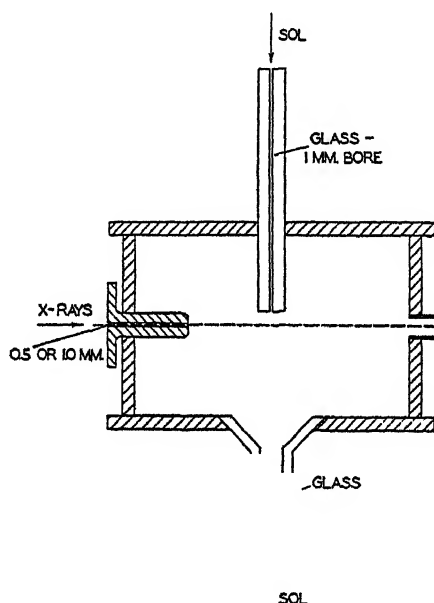


FIG. 16. Camera for the direct x-ray diffraction examination of sols

various sols, and the corresponding solid materials are given in the usual chart form in figure 17, and reproductions of the patterns for cerium dioxide sol and cerium dioxide powder are given in figure 18.

The results are conclusive. In every instance the sol pattern is a composite of the patterns of pure water and of simple oxide or oxide hydrate (or hydroxide). If the sol is weak or the primary crystals very minute, the water bands predominate in the pattern, whereas with stronger sols or larger primary crystals, the water bands appear less pronounced. As in the gels, the dispersed phases in typical hydrosols of the oxides are not polymerized bodies or condensation products but consist essentially of aggregates of minute crystals of simple oxide or of simple hydrate or hy-

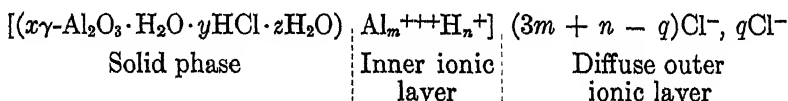
dioxide. In sols containing chloride there is no experimental justification for assuming that it is bound in the form of basic salts or Werner complexes.

IV. SUMMARY

1. The constitution of hydrous oxide gels is deduced from experimental evidence obtained by the application of phase rule and x-ray diffraction techniques to a number of typical oxides. The constitution of the hydrous oxide sols is formulated from the results of potentiometric "titration" of sols with electrolytes and from the direct examination of the sols by x-ray diffraction methods.

2. It is concluded that, in general, gelatinous precipitates of the oxides are not polymerized bodies or condensation products resulting from the splitting off of water from hypothetical metallic hydroxides. Instead, the gels are believed to consist of agglomerates of extremely minute crystals of oxide or simple hydrate (or hydroxide), which hold large amounts of water by adsorption and capillary forces.

3. The particles in typical oxide sols consist essentially of aggregates of minute crystals of hydrous oxide or of simple hydrate (or hydroxide). In sols containing chloride, the latter is not bound in the form of basic salts or Werner complexes in most cases, but is adsorbed in an amount depending on the size and physical character of the primary particles. To account for the properties of positive sols, of which alumina sol from amalgamated aluminum is a typical example, the constitution of the particles may be represented as follows:



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DETERMINATION OF THE IONIZATION AND THERMODYNAMIC PROPERTIES OF WEAK ELECTROLYTES BY MEANS OF CELLS WITHOUT LIQUID JUNCTIONS

HERBERT S. HARNED AND BENTON B. OWEN

Department of Chemistry, Yale University, New Haven, Connecticut

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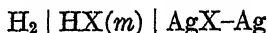
The first application of electromotive force measurements of cells without liquid junctions to the study of weak electrolytes was the calculation of the ionization product, $m_{\text{H}^+}m_{\text{OH}^-}$, and the corresponding activity coefficient function, $\gamma_{\text{H}^+}\gamma_{\text{OH}^-}/a_{\text{H}_2\text{O}}$, for water in salt solutions at 25°C. (15, 38, 46). The corresponding quantities for a weak acid were investigated somewhat later by suitable cells containing an unbuffered solution of acetic acid (43) and various salts. The calculations involved the use of ionization constants determined by other methods, notably the conductance method.

In a later contribution a very thorough investigation of the thermodynamics of such cells containing unbuffered acids was made (41). It was shown that ionization constants and the effect of undissociated acid molecules could be evaluated from the electromotive force data alone. From this stage the use of cells without liquid junctions has expanded rapidly and has been applied to a wide variety of systems which include acids, bases, and ampholytes. Much of this work has been carried out over considerable temperature ranges, and some has involved mixed solvents to introduce the effect of variations in the dielectric constant. ΔF° , ΔH° , and ΔG° for the ionization process at unit activities in pure water, mixed solvent, and salt solutions can be estimated from the proper temperature coefficients. In order to present the results in the simplest possible manner, we will disregard chronological order and develop the subject systematically after a general examination of the fundamental aspects of the method.

1. GENERAL CONSIDERATIONS AND LIMITATIONS OF THE METHOD

The fundamental basis of the method consists in computing the concentration of hydrogen ions (protons + solvated ions) in an unknown solution containing a weak acid, from that of a known concentration of hydrogen ions in a solution of a halogen acid by suitable cell combinations. Its extremes in real solutions, that is to say, solutions other than at zero

ionic strength, will depend on the certainty with which the hydrogen-ion concentration of the halogen acid solution is known. To be explicit, consider the usual method of treatment of the cell,



containing a strong halogen acid solution of molality m . The electromotive force, E , of this cell is given by the equation,

$$\begin{aligned} E &= E_0 - RT/F \ln a_{\text{H}}a_{\text{Cl}} \\ &= E_0 - RT/F \ln \gamma_{\text{H}}\gamma_{\text{Cl}}m_{\text{H}}m_{\text{Cl}} \end{aligned} \quad (1)$$

where $a_{\text{H}}a_{\text{Cl}}$, $\gamma_{\text{H}}\gamma_{\text{Cl}}$, and $m_{\text{H}}m_{\text{Cl}}$ are, respectively, the activity, activity coefficient, and stoichiometric molality products of the acid in the solution. The meaning to be attached to the quantities γ_{H} , γ_{Cl} , m_{H} , and m_{Cl} is largely to be derived from extrathermodynamical knowledge. The subscripts are a convenient symbolism for expressing various combinations of cells and gain significance with the development of the theory and its experimental proof.

All the evidence derivable from modern theory and experiment indicates that hydrochloric acid is a very strong electrolyte. We shall assume that it is completely ionized, and that consequently m_{H} is the sum of the molal concentrations of protons and solvated protons, and m_{Cl} that of the chloride and solvated chloride ions at all ionic strengths. Any actual deviations from this hypothesis of completely ionized hydrochloric acid which may be brought to light by future investigations will necessitate corrections throughout certain of the subsequent computations. However, such corrections will become smaller as the ionic strengths of the solutions decrease and will vanish for extrapolated results at infinite dilution of electrolytes. Since m_{H} and m_{Cl} are the stoichiometric molalities of the sum of all species of hydrogen and chloride ions, $\gamma_{\text{H}}\gamma_{\text{Cl}}$ is the corresponding activity coefficient product of acid. Under these conditions, this quantity conforms to that capable of being computed by the Debye and Hückel theory (8).

These considerations may be applied to one of the cells which will form the subject of the next section, namely,

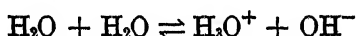


We shall assume that the strong hydroxide, MOH, is completely ionized, so that m_{OH} is the sum of the molalities of the hydroxyl and any hydrated hydroxyl ions present. The electromotive force of this cell is given by equation 1, but in this case the ionization of the weak electrolyte, water, will introduce a fundamental thermodynamic relationship which, when

combined with equation 1, will produce fruitful results. For the ionization constant of water, K_w , we write,

$$K_w = \frac{\gamma_H \gamma_{OH}}{a_{H_2O}^x} m_H m_{OH} \quad (2)$$

where m_H is again the sum of the molalities of the protons and solvated hydrogen ions, $\gamma_H \gamma_{OH}/a_{H_2O}^x$ is an activity coefficient product, and x is unity or greater. By elimination of m_H from equations 1 and 2, we obtain for the electromotive force, E_A , by suitable rearrangement, equations from which K_w , $m_H m_{OH}$, and $\gamma_H \gamma_{OH}/a_{H_2O}^x$ may be computed. The point which should be emphasized so that no misunderstanding may arise is that this method gives K_w exactly and $m_H m_{OH}$ exactly if all strong electrolytes present in the cells are completely ionized. The interpretation of the activity coefficient function depends on the mechanism of the reaction and is not definitely determined by the cell mechanism. If the ionization takes place only according to the reaction,



then the activity coefficient function is

$$\frac{\gamma_{H_3O^+} \gamma_{OH^-}}{a_{H_2O}^2}$$

Since cell measurements alone cannot determine the solvation of ions, we shall employ the more vague but simpler symbolism of equation 2, with $x = 1$.

These considerations hold also for all subsequent computations in cases of cells containing weak acids and ampholytes. Ionization constants may be determined exactly, and ionic concentrations may also be determined exactly provided that all strong electrolytes present in the cells are completely ionized. Future knowledge should make it possible to correct discrepancies due to this latter assumption.

2. THE DETERMINATION OF THE IONIZATION CONSTANT OF WATER

The cells employed for the determination of the ionization constant of water are:

- | | |
|-----|------------------------------------|
| I | $H_2 HX(m) AgX-Ag$ |
| II | $H_2 MOH(m_1), MX(m_2) AgX-Ag$ |
| III | $H_2 HCl(m_1), MX(m_2) AgX-Ag$ |

K_w may be determined from cells I and II (method 1) or from cells II and III (method 2).

Method 1. The electromotive force of cells of type II is given by the equation

$$E_{\text{II}} = E_0 - RT/NF \ln \gamma_{\text{H}} \gamma_{\text{X}} m'_{\text{H}} m'_{\text{X}} \quad (1a)$$

By combination of this equation and equation 2, and rearrangement of the resulting terms in a convenient form, we obtain

$$\frac{(E_{\text{II}} - E_0)NF}{2.303RT} + \log \frac{m'_{\text{X}}}{m'_{\text{OH}}} = \log \frac{\gamma_{\text{H}} \gamma_{\text{OH}}}{a_{\text{H}_2\text{O}}} - \log \gamma_{\text{H}} \gamma_{\text{X}} - \log K_w \quad (3)$$

If the left side of this equation is plotted against the ionic strength, μ , its value at zero μ equals $(-\log K_w)$, since $a_{\text{H}_2\text{O}}$ and all ionic activity coefficients equal unity, and therefore all terms containing them vanish. Cells of this type were employed by Roberts (72), who used equal concentrations of MX and MOH, thus eliminating the second term on the left, and also by a number of investigators (21, 22, 31, 32, 33, 40, 44), who employed ratios of m_{X} to m_{OH} greater than unity. The standard potential, E_0 , may be determined by either cells I or cells III. In either case the extrapolation was made by employing the Debye and Hückel limiting equation.

Method 2. If we subtract the electromotive forces of cells III, E_{III} , from those of cells II, we obtain

$$\frac{(E_{\text{II}} - E_{\text{III}})NF}{2.303RT} = \log \frac{\gamma'_{\text{H}} \gamma'_{\text{X}} m''_{\text{H}} m''_{\text{X}}}{\gamma_{\text{H}} \gamma_{\text{X}} m'_{\text{H}} m'_{\text{X}}} = \log \frac{m''_{\text{H}} m''_{\text{X}}}{m'_{\text{H}} m'_{\text{X}}} \quad (4)$$

where the primes and double primes refer to cells II and III, respectively. The equality to the right introduces the premise that the activity coefficient of the acid is the same in the acid-halide mixtures as in the hydroxide-halide mixtures of the same ionic strength. This assumption is closely approximated, since both the acid and hydroxide are at sufficiently low concentrations ($\sim 0.01 M$ or less). If we substitute for m'_{H} in equation 4 its value derivable from equation 2, we obtain

$$\frac{(E_{\text{II}} - E_{\text{III}})NF}{2.303RT} = \log \frac{m''_{\text{H}} m''_{\text{X}} m'_{\text{OH}}}{m'_{\text{X}}} + \log \frac{\gamma_{\text{H}} \gamma_{\text{OH}}}{a_{\text{H}_2\text{O}}} - \log K_w \quad (5)$$

A suitable extrapolation function can be derived from the limiting law of the theory of Debye and Hückel, for, according to this theory,

$$\ln \frac{\gamma_{\text{H}} \gamma_{\text{OH}}}{a_{\text{H}_2\text{O}}} = - \frac{5.908 \times 10^6}{D^{3/2} T^{3/2}} \sqrt{2\mu} + f(\mu) \quad (6)$$

Substitution in equation 5 gives, upon rearrangement of terms,

$$\frac{(E_{II} - E_{III})NF}{2.303RT} - \log \frac{m''_H m''_X m'_{OH}}{m'_X} + \frac{5.908 \times 10^9}{D^{3/2} T^{1/2}} \sqrt{2\mu} = -\log K_w + f(\mu) \quad (7)$$

Since E_{II} and E_{III} are the measured electromotive forces, and m''_H , m''_{Cl} , m'_{OH} , and m'_{Cl} are known molalities, the left side of the equation is known, and if it is plotted against μ , its value at zero μ is $(-\log K_w)$. Such a plot is nearly linear in the dilute solutions.

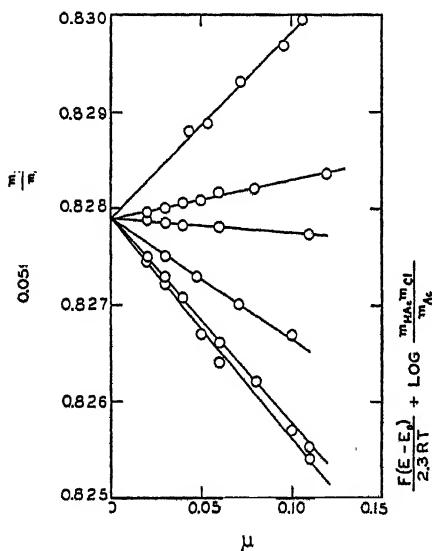


FIG. 1

FIG. 1. Evaluation of $-0.05915 \log K_w$ by measurements in various salt solutions at 25°C. Reading from top to bottom the salts, MX, are cesium chloride, potassium chloride, sodium chloride, barium chloride, lithium bromide, and lithium chloride.

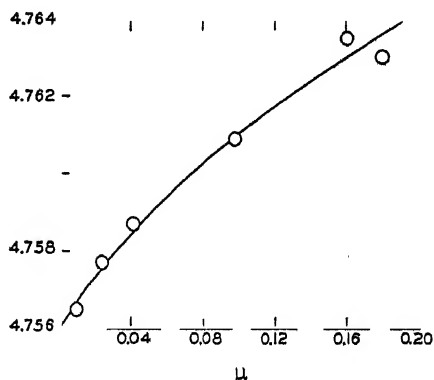


FIG. 2

FIG. 2. Evaluation of the ionization constant of acetic acid at 25°C. Diameters of the circles correspond to 0.02 millivolt.

Numerous examples of extrapolations according to equations 3 and 7 have been given in the literature cited above. One graph which is very informative and which clearly illustrates the high accuracy of the method is shown in figure 1. Here

$$E_{II} - E_0 + 2.303RT/NF \log \frac{m_X}{m_{OH}}$$

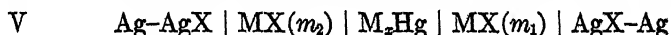
at 25°C. is plotted against the total ionic strength, $\mu = m_X + m_{OH}$. Since the coefficient of the third term equals 0.05915, this quantity according to

equation 3 equals $(0.05915 \log \gamma_{\text{OH}}/\gamma_{\text{X}}a_{\text{H}_2\text{O}} - 0.05915 \log K_w)$ at all values of μ and $(-0.05915 \log K_w)$ when μ equals zero. Results for six salts obtained by as many investigators are plotted. At the lower values of μ these plots are straight lines, and their intercepts at zero μ all lie within 0.05 millivolt. This corresponds to an accuracy of ± 0.1 per cent in the determination of K_w . In all these cases m_{OH} was kept at 0.01, and m_{X} varied.

In addition, we note that at finite values of μ these results can be used to evaluate the interesting stoichiometrical activity coefficient ratio, $\gamma_{\text{OH}}/\gamma_{\text{X}}$, in the salt solutions designated. This result in itself is of considerable interest in connection with the theory of interaction of ions in solutions of finite ionic strength.

3. THE DETERMINATION OF THE ACTIVITY COEFFICIENT FUNCTION, $\gamma_{\text{H}}\gamma_{\text{OH}}/a_{\text{H}_2\text{O}}$, AND THE IONIZATION PRODUCT, $m_{\text{H}}m_{\text{OH}}$, IN SALT SOLUTIONS

In addition to cells I, II, and III, the cells



have been employed in these investigations of the thermodynamics of ionized water in salt solutions. The first determinations of the quantity, $\gamma_{\text{H}}\gamma_{\text{OH}}/a_{\text{H}_2\text{O}}$ (equation 2) were made by Harned (15), Harned and Swindells (46), Harned and James (38), and Harned and Schupp (44) by means of measurements of cells of types III, IV, and V by a method which is essentially the same as that which will now be described.

(1) Cell III may be used to determine $\gamma_{\text{H}}\gamma_{\text{X}}$ at any concentration in a halide solution of any concentration. Therefore, starting with values of $\gamma_{\text{H}}\gamma_{\text{X}}$ at various concentrations at a given constant molality, it is a simple matter to extrapolate to zero acid concentration and obtain $\gamma_{\text{H}}\gamma_{\text{X}}$ at zero concentration of acid in the pure aqueous halide solution (16).

(2) Similarly, $\gamma_{\text{M}}\gamma_{\text{OH}}/a_{\text{H}_2\text{O}}$ at zero hydroxide-ion concentration, that is to say in pure salt solution, may be obtained from cells of type IV.

(3) From cells of type V, $\gamma_{\text{M}}\gamma_{\text{X}}$ in the pure aqueous salt solution at the same molality may be determined.

(4) Since all these quantities have been evaluated in the pure halide solution, they may be combined without any loss of accuracy. Thus, by multiplying the first two and dividing by the third, we obtain

$$(\gamma_{\text{H}}\gamma_{\text{X}}) \left(\frac{\gamma_{\text{M}}\gamma_{\text{OH}}}{a_{\text{H}_2\text{O}}} \right) \left(\frac{1}{\gamma_{\text{M}}\gamma_{\text{X}}} \right) = \frac{\gamma_{\text{H}}\gamma_{\text{OH}}}{a_{\text{H}_2\text{O}}} \quad (8)$$

which gives us the desired quantity at one salt concentration.

This method is theoretically sound and yields good results but requires measurements of the more cumbersome flowing amalgam cells and incorporates the combined errors of the three types of cells. This method has been superseded by a procedure which involves cells of types II and III.

The equation for cells III may be written,

$$\log \gamma_{\text{H}} \gamma_{\text{X}} = -\frac{F}{2.303RT} (E_{\text{III}} - E_0) - \log m_{\text{H}}'' m_{\text{X}}'' \quad (9)$$

Equation 3 may be stated in the form

$$\log \frac{\gamma_{\text{H}} \gamma_{\text{OH}}}{a_{\text{H}_2\text{O}}} = \frac{F}{2.303RT} (E_{\text{II}} - E_0) + \log \gamma_{\text{H}} \gamma_{\text{X}} + \log \frac{m_{\text{X}}'}{m_{\text{OH}}} + \log K_w \quad (10)$$

from which $\gamma_{\text{H}} \gamma_{\text{OH}}/a_{\text{H}_2\text{O}}$ may be determined from a knowledge of the standard potential, E_0 , and the values of $\gamma_{\text{H}} \gamma_{\text{X}}$ derivable from equation 9. It is convenient to combine these equations and compute $\gamma_{\text{H}} \gamma_{\text{OH}}/a_{\text{H}_2\text{O}}$ by means of the relation,

$$\log \gamma_{\text{H}} \gamma_{\text{OH}}/a_{\text{H}_2\text{O}} = \frac{F}{2.303RT} (E_{\text{II}} - E_{\text{III}}) - \log \frac{m_{\text{H}}'' m_{\text{X}}'' m_{\text{OH}}'}{m_{\text{X}}} + \log K_w \quad (11)$$

Finally, combination with equation 2 gives

$$-\log m_{\text{H}} m_{\text{OH}} = \frac{F}{2.303RT} (E_{\text{II}} - E_{\text{III}}) - \log \frac{m_{\text{H}}'' m_{\text{X}}'' m_{\text{OH}}'}{m_{\text{X}}} \quad (12)$$

from which the ionization, $m_{\text{H}} m_{\text{OH}}$, in the halide solutions may be obtained directly from the molalities of the electrolytes and the electromotive forces.

In the investigations above mentioned, $\gamma_{\text{H}} \gamma_{\text{OH}}/a_{\text{H}_2\text{O}}$ and $m_{\text{H}} m_{\text{OH}}$ have been evaluated from 0° to 50°C. in cesium (44), potassium (32), sodium (40), and lithium (21) chloride solutions, potassium (33), sodium (33), and lithium (22) bromide solutions, and barium (31) chloride solutions. In these and other contributions (18) the results have been tabulated and discussed. The methods of obtaining the derived heat data have also received attention. Since the results have been discussed in detail in the above contribution (18), further specialized discussion of them will be omitted.

On the other hand, there is something to be said regarding the accuracy of the determination of the ionization, $m_{\text{H}} m_{\text{OH}}$, in the halide solutions. It has been shown (section 1) that if all the electrolytes employed in the cells are completely ionized at all concentrations, then $m_{\text{H}} m_{\text{OH}}$ is exactly determined. Evidence from thermodynamic and conductance data shows that hydrochloric acid, hydrobromic acid, and the alkaline halides are very strong electrolytes, so that corrections in the values of $m_{\text{H}} m_{\text{OH}}$ from this source will be small. The hydroxides are also strong electrolytes, but

there is evidence that lithium hydroxide and, to a less extent, sodium hydroxide form associated ionic pairs. Potassium and cesium hydroxides are very strong. The fact that the plot of equivalent conductance against square root of the concentration for lithium hydroxide does not lie below the Onsager slope at any concentration indicates that any corrections in these results due to ionic association will not be of large magnitude.

4. IONIZATION CONSTANTS OF WEAK ACIDS AND BASES

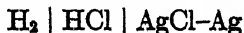
The simplest and most direct determination of the ionization constant of a weak acid is based upon measurements of the electromotive forces of cells of the type (24, 25)



Although such cells have been limited to the determination of dissociation constants only, they are peculiarly well adapted to this purpose. Buffer action permits accurate and easy measurements at small hydrogen-ion concentrations and at relatively low ionic strengths. The necessary extrapolation is practically linear except when carried out in media of low dielectric constant and does not require numerous experimental data. The concentrations of the weak acid, HR, and the two salts, MR and MCl, are made approximately equal, and the cation M is usually sodium or potassium. The use of chlorides and the silver-silver chloride electrode has many practical advantages, but other combinations will suggest themselves in special cases. The electromotive force of this cell is given by the same equation as for cells I, II, and III, namely,

$$E = E_0 - \frac{2.3RT}{F} \log \gamma_{\text{H}} \gamma_{\text{Cl}} m_{\text{H}} m_{\text{Cl}} \quad (13)$$

As before, E_0 is the electromotive force of the cell



at unit activity. The product, $\gamma_{\text{H}} m_{\text{H}}$, can be eliminated by combination with the expression for the ionization of the weak electrolyte,

$$K_{\text{A}} = \frac{\gamma_{\text{H}} \gamma_{\text{R}}}{\gamma_{\text{HR}}} \frac{m_{\text{H}} m_{\text{R}}}{m_{\text{HR}}}$$

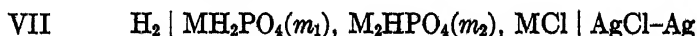
Thus the equation

$$\frac{(E - E^0)F}{2.3RT} + \log \frac{m_{\text{Cl}} m_{\text{HR}}}{m_{\text{R}}} = -\log K_{\text{A}} - \log \frac{\gamma_{\text{Cl}} \gamma_{\text{HR}}}{\gamma_{\text{R}}} \quad (14)$$

is obtained. The terms of the left-hand side are all experimentally determinable, since $m_{\text{Cl}} = m_3$, $m_{\text{HR}} = m_1 - m_{\text{H}}$, $m_{\text{R}} = m_2 + m_{\text{H}}$, and

m_H may be estimated with sufficient accuracy by a short series of successive approximations explained elsewhere (24, 57, 67). The last term on the right contains the logarithm of the activity coefficient ratio of two univalent ions and the logarithm of the activity coefficient of a neutral molecule, both of which are known to vary linearly with the ionic strength at high dilution. Accordingly, a plot of the left-hand member of equation 14 against the ionic strength, μ , permits the determination of $-\log K_A$ by extrapolation to $\mu = 0$. Figure 2 illustrates the extrapolation by which the dissociation constant of acetic acid is evaluated at 25°C. (24). The extrapolated value of K_A is 1.754×10^{-5} , which is in almost exact agreement with the value 1.758×10^{-5} obtained by conductance measurements (53) and 1.75×10^{-5} derived from electromotive force data on unbuffered solutions (41). Ionization constants of the order of 10^{-3} or 10^{-2} cannot be determined by this method with the same precision because of the increased difficulty of estimating m_H for use in equation 14 (14).

In the case of polybasic acids the extrapolation function is complicated by stepwise dissociation and the presence of polyvalent ions, but this is of little practical importance if the ratios of the constants of the several dissociation processes are greater than 10^3 or 10^4 . The second ionization constant of phosphoric acid is especially well suited for determination by this method and will be used to outline the details of the calculations (57). The cel. may be represented by



and its electromotive force by equation 1. The second dissociation constant of phosphoric acid is given by

$$K_{2A} = \frac{\gamma_H \gamma_{\text{HPO}_4}}{\gamma_{\text{H}_2\text{PO}_4}} \frac{m_H m_{\text{HPO}_4}}{m_{\text{H}_2\text{PO}_4}} \quad (15)$$

which leads to

$$\frac{(E - E_0)F}{2.303RT} + \log \frac{m_{\text{Cl}} m_{\text{H}_2\text{PO}_4}}{m_{\text{HPO}_4}} = -\log K_{2A} - \log \frac{\gamma_{\text{Cl}} \gamma_{\text{H}_2\text{PO}_4}}{\gamma_{\text{HPO}_4}} \quad (16)$$

by elimination of $\gamma_H m_H$ with equation 1. The last term on the right contains the activity coefficients of two univalent ions in the numerator and of a bivalent ion in the denominator. Application of the Debye-Hückel equation to this term allows its replacement by $-2S\sqrt{\mu} \pm \beta\mu$ at high dilution. Combining all known quantities in the left member, equation 16 becomes

$$\left[\frac{(E - E_0)F}{2.303RT} + \log \frac{m_{\text{Cl}} m_{\text{H}_2\text{PO}_4}}{m_{\text{HPO}_4}} + 2S\sqrt{\mu} \right] = -\log K_{2A} \pm \beta\mu \quad (17)$$

The value of the constant $\pm\beta$ is not determined by present theory, but this is immaterial because it is introduced solely to indicate that a plot of the bracketed member of equation 17 against μ should be linear at high dilution and permit the evaluation of $-\log K_{2A}$ by extrapolation. Figure 3 illustrates the extrapolation at 25°C. (57).

It is interesting to note that, in the phosphate buffer solutions employed, the value of m_H is of the order 10^{-7} , which is so small relative to m_1 and m_2 that it may be disregarded in computing $m_{H_2PO_4}$ and m_{HPO_4} . If, however, m_H is very much less than 10^{-7} , the effects of the hydroxyl-ion concentration and hydrolysis of the acid anion must be taken into account. In general practice it will be found that both m_H and m_{OH} may be neglected if $\frac{m_1}{m_2} \simeq 1$ and K is between 10^{-5} and 10^{-9} .

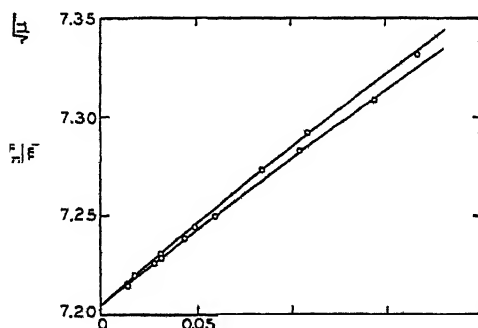


FIG. 3. Evaluation of the second ionization constant of phosphoric acid at 25°C. Lower curve: sodium salts, $m_1 = m_2$. Upper curve: monosodium phosphate and dipotassium phosphate, $4m_1 = 3m_2$.

The dissociation constant of HBO_2 , or perhaps more properly the first dissociation constant of H_3BO_3 , is so small ($ca. 6 \times 10^{-10}$) that m_{OH} must be considered at high dilution. In this case $m_{HR} = m_1 + m_{OH}$, $m_R = m_2 - m_{OH}$, and $m_{OH} \simeq K_h \frac{m_2}{m_1}$ can be estimated with sufficient accuracy from a rough approximation of the hydrolysis constant, K_h , of the acid anion. The tendency of boron to form complex acids in concentrated solution results in a peculiar plot of the extrapolation function of equation 14. Figure 4 illustrates its behavior at 25°C. (67). The ratio m_1/m_2 is 1 in the upper curve, about 1.2 in the short central curve, and about 2.7 in the lower curve. It should be remarked that the upper curve is practically horizontal below $\mu \simeq 0.01$, which makes extrapolation of that series unnecessary beyond this point. Furthermore, equation 14 may be used to determine E_0 once K_A has been evaluated. The combination of

these circumstances and the stability of iodides in alkaline solutions has made it possible to determine E_0 for the silver-silver iodide electrode (69) with much greater ease than by the orthodox use of cells containing dilute hydriodic acid solutions. The use of buffer solutions has been found advantageous in determining other standard electrode potentials (3, 70) as well.

The dissociation constants of weak bases can be determined by a method analogous to that used for acids. Since silver chloride is soluble in ammonia and most amines, some substitute for the silver-silver chloride electrode must be used in many basic systems. The sodium amalgam electrode is known (42) to give results comparable with those of the silver-silver chloride electrode in a system where both can be used, and the use of thallium amalgam has been suggested (73). The silver-silver

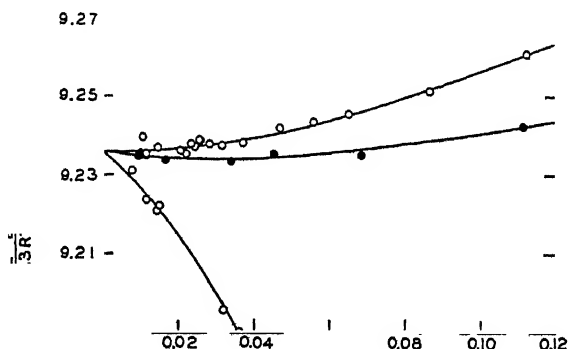


FIG. 4. Evaluation of the ionization constant of boric acid at 25°C. The ratio $m_{\text{HBO}_2}/m_{\text{BO}_2}$ is 1 in the upper curve, 1.18 in the center curve, and 2.69 in the lower curve.

iodide electrode is the most convenient one for the purpose and will be used to illustrate the method.

The cell can be written



and its electromotive force can be expressed by equation 1 if the substitution of I^- for Cl^- is taken into account. The unknown factor $\gamma_{\text{H}}m_{\text{H}}$ can be eliminated by the introduction of the expressions

$$K_w = \frac{\gamma_{\text{H}}\gamma_{\text{OH}}}{a_{\text{H}_2\text{O}}} m_{\text{H}}m_{\text{OH}} \quad (2)$$

and

$$K_B = \frac{\gamma_{\text{B}}\gamma_{\text{OH}}}{\gamma_{\text{BOH}}} m_{\text{B}}m_{\text{OH}} \quad (18)$$

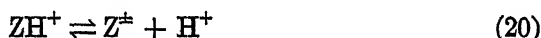
The resulting extrapolation function can be written

$$\left[\frac{(E - E_0)F}{2.303RT} + \log K_w + \log \frac{m_B m_I}{m_{BOH}} - S\sqrt{\mu} \right] = \log K_B \pm \beta\mu \quad (19)$$

after $-S\sqrt{\mu} \pm \beta\mu$ has been substituted for $\log \gamma_{BI}/\gamma_{BOH}$. Preliminary measurements on ammonia buffers (68) resulted in a value for K_B of the expected order of magnitude. The high vapor pressure of ammonia and its action upon the glass of the cells make it much less amenable to precise investigation than weak acids, so that it has not yet received the attention it deserves. The most reliable values for the dissociation constants of bases are probably the values of K_B derived for the basic dissociation of ampholytes discussed in the next section.

5. DETERMINATION OF THE IONIZATION CONSTANTS OF AMPHOLYTES

The determination of the ionization of the most important ampholyte, water, by cells without liquid has been discussed in section 2. The other ampholytes that have been investigated by this method have all been aliphatic amino acids. The neutral molecules of these compounds in solution have been shown (2, 5, 9, 79) to be mainly zwitter ions, or amphions, bearing a positive and negative charge. If such molecules are indicated by Z^\pm , the acidic and basic dissociation of a simple amino acid may be represented conveniently by



and



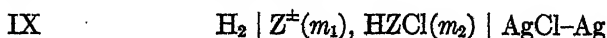
and the corresponding ionization constants by (5, 42)

$$K_A = \frac{\gamma_Z \gamma_H}{\gamma_{ZH}} \frac{m_Z m_H}{m_{ZH}} \quad (22)$$

and

$$K_B = \frac{\gamma_Z \gamma_{OH}}{\gamma_{ZOH}} \frac{m_Z m_{OH}}{m_{ZOH}} \quad (23)$$

The most convenient determination of acidic ionization is performed with cells containing approximately equal concentrations of amino acid and its hydrochloride. Thus for the cell



the electromotive force is given by equation 1, and elimination of $\gamma_H m_H$ by equation 22 leads to

$$\frac{(E - E_0)F}{2.3RT} + \log \frac{m_{Cl} m_{ZH}}{m_Z} + \log \frac{\gamma_{Cl} \gamma_{ZH}}{\gamma_Z} = -\log K_A \quad (24)$$

The last term of the left side may be replaced by $-2S\sqrt{\mu} \pm \beta\mu$ and the unknown linear term transposed to give an extrapolation function,

$$\frac{(E - E^0)F}{2.3RT} + \log \frac{m_{\text{Cl}}m_{\text{ZH}}}{m_{\text{Z}}} - 2S\sqrt{\mu} = -\log K_A \pm \beta\mu \quad (25)$$

very similar to that used for phosphoric acid. Since $m_{\text{Cl}} = m_2$, $m_{\text{Z}} = m_1 + m_{\text{H}}$, and $m_{\text{ZH}} = m_2 - m_{\text{H}}$, the concentration term may be evaluated by successive approximations from a preliminary value of K_A obtained by neglecting m_{H} altogether. Convergence of successive approximations is rather slow for the amino acids investigated to date because their values

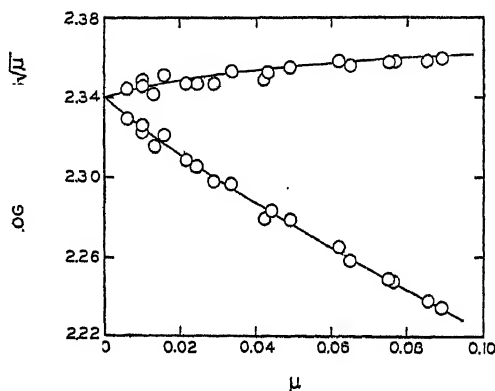


FIG. 5. Determination of the acidic ionization constant of *dl*-alanine at 25°C. In the upper curve $-2S\sqrt{\mu}$ has been replaced by experimental values of $\log \gamma_{\text{H}}\gamma_{\text{Cl}}$ in pure sodium chloride solutions.

of K_A are of the order 10^{-3} to 10^{-2} . It is perhaps more satisfactory to rewrite equation 1 as

$$-\log m_{\text{H}} = \frac{(E - E_0)F}{2.3RT} + \log m_{\text{Cl}} + \log \gamma_{\text{H}}\gamma_{\text{Cl}} \quad (26)$$

and estimate m_{H} with the help of the approximation

$$\log \gamma_{\text{H}}\gamma_{\text{Cl}} = -2S\sqrt{\mu}$$

Figure 5 illustrates the use of equation 25 in evaluating K_A for *dl*-alanine (60). At each temperature the lower curve is the plot of the left-hand member of equation 25 against μ . The upper, almost horizontal, curve represents an alternative function obtained by replacing $-2S\sqrt{\mu}$ in equation 25 by known values of $\log \gamma_{\text{H}}\gamma_{\text{Cl}}$ in pure aqueous solutions at the ionic strength and temperatures in question. Since both extrapolation functions must give the same value of $-\log K_A$, their difference in slopes is of some practical advantage in accurately locating the common intercept.

The basic ionization constants of ampholytes can be determined by cells of the type



in which the concentrations of the constituents are usually made equal. MZOH represents a convenient alkali (sodium or potassium) salt of the ampholyte and MCl the corresponding chloride. Strictly speaking, the symbol MZOH indicates a hydrated form of the salt, which is here used for convenience in exposition. The question of hydration affects the interpretation of K_B but not its numerical evaluation.

Eliminating $\gamma_H m_H$ and $\gamma_{OH} m_{OH}$ between equations 1 and 23 and the expression for the ionization of water, we obtain

$$\frac{(E - E_0)F}{2.3RT} + \log \frac{m_{Cl} m_Z}{m_{ZOH}} + \log K_w = \log K_B - \log \frac{\gamma_{Cl} \gamma_Z a_{H_2O}}{\gamma_{ZOH}} \quad (27)$$

3

log

-4.20

-4.25

0.02

0.06

FIG. 6. Evaluation of the basic ionization constant of glycine at 25°C. and 35°C. (upper curve)

The last term on the right involves only neutral molecules and the ratio of two similar ionic activity coefficients. It is therefore linear in μ at high dilution.

Figure 6 illustrates the use of this extrapolation function to evaluate the basic ionization constant of glycine (66).

6. NUMERICAL VALUES OF IONIZATION CONSTANTS AND THE DERIVED THERMODYNAMIC FUNCTIONS, ΔH^0 , ΔS^0 , AND ΔC_p^0

Tables 1 and 1A summarize the ionization constants obtained by these methods.¹ Only observed values free from temperature smoothing are

¹ While this article was in press, the ionization constants of oxalic acid in water and some methanol-water mixtures were reported by H. C. Parton and R. C. Gibbons (Trans. Faraday Soc. **35**, 542 (1939)) and H. N. Parton and A. J. C. Nicholson (Trans. Faraday Soc. **35**, 546 (1939)).

recorded. In the case of water "best" values from various determinations (31) are given. Two of the acids in table 1 have been independently studied at 25°C. The values $K_A = 1.77 \times 10^{-4}$ for formic acid and $K_A = 1.75 \times 10^{-5}$ for acetic acid were obtained by Harned and Owen (41) in the first calculation of ionization constants from cells without liquid junctions.

There is a discrepancy of 1 or 2 per cent between the independently determined constants of *dl*-alanine that appear in table 1 and those given in table 1A. Whenever the absolute magnitude of K_A or K_B is required the data of table 1 are to be preferred, because the results in table 1A were obtained on very limited quantities of the amino acids and without complete exclusion of air during the cell manipulation. On the other hand, the thermochemical quantities derived from the temperature coefficients of K_A and K_B for alanine are possibly more accurately derived from table 1A because of the longer temperature range.

Precise conductometric determinations, in which proper account was taken of ionic interaction, are now available for a number of acids. *For purposes of comparison all conductometric ionization constants have been converted to a molality basis* by multiplication of the values given in the literature by the specific volume of water at the proper temperature. MacInnes and Shedlovsky (53) found $K_A = 1.758 \times 10^{-5}$ for acetic acid at 25°C. Belcher (4) recently obtained $K_A = 1.347 \times 10^{-5}$ for propionic acid and $K_A = 1.512 \times 10^{-5}$ for *n*-butyric acid at 25°C.

Saxton and Langer (74) and MacInnes, Shedlovsky, and Longworth (54) reported the almost identical values 1.400×10^{-3} and 1.401×10^{-3} for chloroacetic acid at 25°C. These figures are certainly to be preferred to the lower value in table 1, which required the use of a secondary standard electrode (quinhydrone), but the temperature coefficient and thermal quantities derived from the electromotive force study are probably correct. Martin and Tartar (55) obtained $K_A = 1.391 \times 10^{-4}$ for lactic acid at 25°C. by the usual conductance study over a wide concentration range, and then extended their calculations to other temperatures by measurements on 0.001 normal solutions of lactic acid, potassium lactate, hydrochloric acid, and potassium chloride. Their values at 0° and 50°C. are 1.317×10^{-4} and 1.290×10^{-4} , respectively.

Among the remaining acids in table 1 only phosphoric and sulfuric acids have had their ionization constants estimated by modern conductometric methods. Making use of the data of Abbott and Bray (1) and Noyes and Eastman (62), Sherrill and Noyes (75) obtained $K_{1A} = 8.31 \times 10^{-3}$ for phosphoric acid at 18°C. From the data of Noyes and Stewart (63) they derived the value $K_{2A} = 1.18 \times 10^{-2}$ for sulfuric acid at 25°C. Taking the above comparisons as a whole, the agreement to be expected

TABLE I
Observed ionization constants

| ELECTROLYTE | CONSTANTS | | | | | | | | | | | | | REFERENCE |
|--|-----------|--------|--------|--------|--------|-------|--------|--------|-------|-------|-------|-------|-------|-----------|
| | 0°C. | 5°C. | 10°C. | 15°C. | 20°C. | 25°C. | 30°C. | 35°C. | 40°C. | 45°C. | 50°C. | 55°C. | 60°C. | |
| Formic acid, $K_A \times 10^4$ | 1.638 | 1.691 | 1.728 | 1.749 | 1.765 | 1.772 | 1.768 | 1.747 | 1.716 | 1.685 | 1.650 | 1.607 | 1.551 | (28) |
| Acetic acid, $K_A \times 10^5$ | 1.657 | 1.700 | 1.729 | 1.745 | 1.753 | 1.754 | 1.750 | 1.728 | 1.703 | 1.670 | 1.633 | 1.589 | 1.542 | (25) |
| Propionic acid, $K_A \times 10^5$... | 1.274 | 1.305 | 1.326 | 1.336 | 1.338 | 1.336 | 1.326 | 1.310 | 1.280 | 1.257 | 1.229 | 1.195 | 1.160 | (27) |
| n-Butyric acid, $K_A \times 10^5$... | 1.563 | 1.574 | 1.576 | 1.569 | 1.542 | 1.515 | 1.484 | 1.439 | 1.395 | 1.347 | 1.302 | 1.252 | 1.199 | (45) |
| Chloroacetic acid, $K_A \times 10^4$... | 1.523 | 1.488 | 1.440† | | | 1.379 | 1.308† | | 1.230 | | | | | (78) |
| Lactic acid, $K_A \times 10^4$ | 1.287 | 1.361* | | | | 1.374 | | 1.336§ | | | 1.270 | | | (61) |
| Glycolic acid, $K_A \times 10^4$ | 1.334 | 1.427* | | | | 1.475 | | 1.471§ | | | 1.415 | | | (59) |
| Sulfuric acid, $K_2A \times 10^3$ | 1.48 | 1.43 | 1.39 | 1.34 | 1.27 | 1.20 | 1.13 | 1.05 | 0.97 | 0.89 | 0.79 | 0.70 | 0.60 | (14) |
| Phosphoric acid, $K_1A \times 10^3$... | 8.968 | 8.394* | | | | 7.516 | | 6.531§ | | | 5.495 | | | (58) |
| | | | | | 6.056 | 6.226 | 6.349 | 6.430 | 6.471 | 6.475 | 6.439 | | | (57) |
| Boric acid, $K_1A \times 10^{10}$ | | 3.63 | 4.17 | 4.72 | 5.26 | 5.79 | 6.34 | 6.86 | 7.38 | | 8.32 | | | (67, 69) |
| Water, $K_w \times 10^{14}$ | 0.1133 | 0.1846 | 0.2920 | 0.4503 | 0.6809 | 1.008 | 1.468 | 2.089 | 2.917 | 4.018 | 5.474 | 7.297 | 9.614 | (31) |
| Glycine, $K_A \times 10^5$ | | 3.94 | 4.68 | | 4.31 | 4.47 | 4.59 | | 4.81 | | | | | (66) |
| | | | | 5.12 | 5.57 | 6.04 | 6.52 | 6.98 | 7.43 | 7.87 | | | | (66) |
| dL-Alanine, $K_A \times 10^5$ | | | | | 4.47 | 4.57 | 4.66 | 4.71 | 4.74 | 4.76 | | | | (60) |
| | | | | | 6.90 | 7.47 | 8.08 | 8.61 | 9.10 | 9.60 | | | | (60) |
| Acetic acid in: | | | | | | | | | | | | | | |
| 10 per cent methanol, $K_A \times 10^5$ | 1.138 | | 1.200 | | 1.242 | 1.247 | 1.237 | | 1.214 | | | | | (30) |
| 20 per cent methanol, $K_A \times 10^5$ | 7.38 | | 7.94 | | 8.24 | 8.34 | 8.30 | | 8.19 | | | | | (30) |
| 20 per cent dioxane, $K_A \times 10^6$ | 4.75 | 4.87 | 4.98 | 5.05 | 5.09 | 5.11 | 5.08 | 5.03 | 4.95 | 4.86 | 4.73 | | | (19) |
| 45 per cent dioxane, $K_A \times 10^7$ | 4.78 | 4.89 | 4.96 | 4.96 | 4.96 | 4.93 | 4.86 | 4.75 | 4.61 | 4.44 | 4.28 | | | (19) |
| 70 per cent dioxane, $K_A \times 10^8$ | 4.75 | 4.83 | 4.89 | 4.83 | 4.83 | 4.78 | 4.69 | 4.56 | 4.42 | 4.22 | 4.05 | | | (19) |

* At 12.5°C. † At 18°C. § At 37.5°C.

between the modern conductance and electromotive force determinations of ionization constants is of the order of 1 per cent.

Space will not permit comparison with all of the estimates of ionization constants obtained from cells involving liquid junctions, but we will present some recent values to show the order of the agreement that can be expected from modern technique and calculations in accord with the interionic attraction theory. The values obtained with liquid junctions

TABLE 1A
Observed ionization constants (76)

| ELECTROLYTE | CONSTANTS | | | | |
|--|-----------|---------|-------|---------|-------|
| | 1°C. | 12.5°C. | 25°C. | 37.5°C. | 50°C. |
| <i>dl</i> -Alanine, $K_A \times 10^3$ | 3.75 | 4.14 | 4.49 | 4.68 | 4.66 |
| $K_B \times 10^6$ | 4.83 | 6.10 | 7.40 | 8.73 | 9.86 |
| <i>dl</i> - α -Amino- <i>n</i> -butyric acid, $K_A \times 10^3$ | 4.63 | 4.90 | 5.18 | 5.15 | 5.05 |
| $K_B \times 10^6$ | 4.25 | 5.50 | 6.81 | 8.22 | 9.38 |
| <i>dl</i> - α -Amino- <i>n</i> -valeric acid, $K_A \times 10^3$ | 4.21 | 4.57 | 4.81 | 4.91 | 4.86 |
| $K_B \times 10^6$ | 4.04 | 5.18 | 6.47 | 7.64 | 8.63 |
| <i>dl</i> -Norleucine, $K_A \times 10^3$ | 4.04 | 4.41 | 4.62 | 4.74 | 4.70 |
| $K_B \times 10^4$ | 4.41 | 5.62 | 6.87 | 8.05 | 9.16 |
| α -Aminoisobutyric acid, $K_A \times 10^3$ | 3.81 | 4.17 | 4.40 | 4.46 | 4.41 |
| $K_B \times 10^4$ | 1.14 | 1.38 | 1.61 | 1.84 | 1.99 |
| <i>dl</i> -Valine, $K_A \times 10^3$ | 4.79 | 5.05 | 5.18 | 5.11 | 4.90 |
| $K_B \times 10^6$ | 3.24 | 4.21 | 5.27 | 6.28 | 7.28 |
| <i>dl</i> -Leucine, $K_A \times 10^3$ | 4.14 | 4.49 | 4.70 | 4.71 | 4.65 |
| $K_B \times 10^6$ | 3.57 | 4.52 | 5.60 | 6.71 | 7.59 |
| <i>dl</i> -Isoleucine, $K_A \times 10^3$ | 4.32 | 4.59 | 4.81 | 4.82 | 4.66 |
| $K_B \times 10^6$ | 3.61 | 4.57 | 5.77 | 6.79 | 7.85 |

recorded in table 2 were determined by Larsson and Adell (52) at 18°C. The corresponding values from cells without liquid junctions were interpolated to this temperature by means of the constants K_θ and θ given in table 3.

The results in table 1 may be expressed with an average accuracy of the order of 0.002 in $\log K$ by the equation of Harned and Embree (29),

$$\log K = \log K_\theta - p(t - \theta)^2 \quad (28)$$

The concordance of this equation with the data in table 1A is within 0.003 in $\log K$, on the average, with occasional differences as high as 0.007.

K_θ is the value of K at its maximum, θ is the temperature at which K is a maximum, p has the value of $5 \times 10^{-5} \text{ deg.}^{-2}$ except for boric acid, in which case 8×10^{-5} was used. The temperature is expressed at $t^\circ\text{C}$. Values of the parameters of this equation are recorded in table 3 for all of the electrolytes in tables 1 and 1A except sulfuric acid and water. These last two electrolytes cannot be satisfactorily expressed by an equation of the form of equation 28. In addition to the systems in which the solvent is pure water, all of the results obtained in aqueous mixed solvents by cells without liquid junctions are included at the bottom of table 3. Equation 28 also reproduces these results within their apparent experimental uncertainties. The practical effectiveness of this equation will be further demonstrated in the next section by table 5 in conjunction with equation 54.

TABLE 2

Comparison of ionization constants at 18°C. derived from cells with and without liquid junctions

| ACID | WITH LIQUID JUNCTIONS | WITHOUT LIQUID JUNCTIONS |
|------------------------|------------------------|--------------------------|
| Formic..... | 1.79×10^{-4} | 1.76×10^{-4} |
| Acetic..... | 1.73×10^{-5} | 1.75×10^{-5} |
| Propionic..... | 1.32×10^{-5} | 1.34×10^{-5} |
| <i>n</i> -Butyric..... | 1.53×10^{-5} | 1.56×10^{-5} |
| Chloroacetic..... | 1.49×10^{-5} | 1.44×10^{-5} |
| Lactic..... | 1.38×10^{-4} | 1.37×10^{-4} |
| Glycolic..... | 1.462×10^{-4} | 1.355×10^{-4} |

The heat content and heat capacity changes of the ionization reaction at unit activities are given by the equations

$$\Delta H^0 = -4.575 \times 10^{-4} T^2 (t - \theta) \quad (29)$$

$$\Delta C_p^0 = -4.575 \times 10^{-4} T (T + 2(t - \theta)) \quad (30)$$

derived by differentiation of equation 28. The free energy and subsequently the entropy changes may be obtained from the customary fundamental thermodynamic relations

$$\Delta F^0 = -2.3026RT \log K \quad (31)$$

$$\Delta S^0 = \frac{\Delta H^0 - \Delta F^0}{T} \quad (32)$$

The equation employed in the estimation of the thermochemical quantities for sulfuric acid is the one given by Hamer (14)

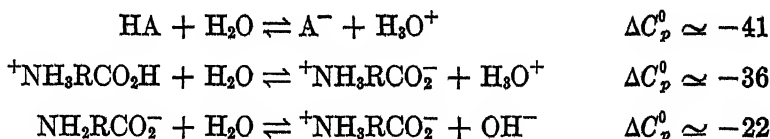
$$\log K_{2A} = -1387.6/T + 1.15612 \log T - 1.355 \times 10^{-5} T - 3.8182 \times 10^{-5} T^2 + 3.27632 \quad (33)$$

For the ionization of water we employed the equation

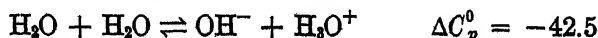
$$\log K_w = -4787.3/T - 7.1321 \log T - 0.010365T + 22.801 \quad (34)$$

given by Harned and Hamer (32). This equation satisfactorily expresses the selected values given in table 1 from 10° to 35°C., but we believe it should not be employed outside this range. This limitation in the use of equation 34 undoubtedly introduces considerable uncertainty in the values of ΔH^0 , ΔC_p^0 , and ΔS^0 derived from it. This error, due to empirical curve fitting, is inherent in all determinations of thermochemical data from electromotive force measurements, but, other things being equal, it is minimized by studying as large a temperature range as possible. A fair idea of the magnitude of the curve-fitting error can be had by comparing the values in table 3 with those obtained from equations of the form of equation 34 as reported in the original experimental investigations. These values at 25°C. are $\Delta H^0 = -112$, $\Delta C_p^0 = -33.9$ for acetic acid, $\Delta H^0 = -168$, $\Delta C_p^0 = -37.7$ for propionic acid, $\Delta H^0 = -1170$, $\Delta C_p^0 = -34.9$ for chloroacetic acid, and $\Delta H_A^0 = 1159$, $\Delta C_{pA}^0 = -30.6$, $\Delta H_B^0 = 2765$, $\Delta C_{pB}^0 = -22.2$ for glycine. With the exceptions of water and sulfuric acid already noted, all of the electrolytes in the tables have been expressed in terms of equation 28. An elaboration of this discussion of the uncertainties of derived quantities, with particular reference to equation 28, can be found in the papers by Walde (77) and Pitzer (71). The latter paper will be given consideration later, because it contains original experimental results and the proposal of a simple two-constant equation to replace equation 28.

One significant generalization, which shows the importance of determining ionization constants as a function of temperature, may be immediately obtained by inspection of table 3. It is clear that no simple inference is to be drawn from the values of ΔF^0 , ΔH^0 , and ΔS^0 , but ΔC_p^0 exhibits some interesting regularities. With the exception of HSO_4^- , H_3PO_4 , and H_2PO_4^- , the results may be arranged in three groups, corresponding to the type reactions,



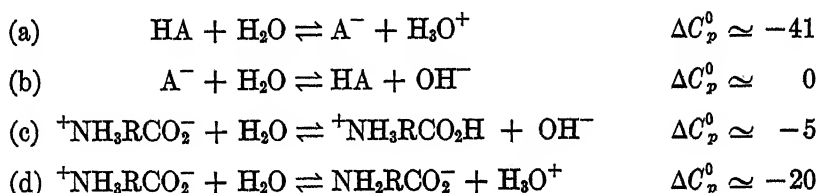
This relationship may be stated in a more significant way by comparing all of the results with a common reference reaction. For this comparison we have chosen the ionization of water,



| | | | | | | | | |
|--------------------------------------|------|-------|-------|-------|-------|------|-------|-------|
| <i>dl</i> -Leucine (K_A)..... | 0-50 | 35.4 | 2.324 | 2.329 | 3176 | 423 | -37.8 | -9.2 |
| (K_B)..... | 0-50 | 93.0 | 4.022 | 4.253 | 5800 | 2765 | -22.1 | -10.2 |
| <i>dl</i> -Isoleucine (K_A)..... | 0-50 | 32.4 | 2.317 | 2.320 | 3164 | 301 | -38.6 | -9.6 |
| (K_B)..... | 0-50 | 93.8 | 4.009 | 4.246 | 5791 | 2797 | -21.9 | -10.0 |
| Acetic acid in: | | | | | | | | |
| 10 per cent methanol..... | 0-40 | 27.0 | 4.904 | 4.905 | 6690 | 81 | -40.1 | -22.2 |
| 20 per cent methanol..... | 0-40 | 31.5 | 5.079 | 5.081 | 6930 | 264 | -38.9 | -22.4 |
| 20 per cent dioxane..... | 0-50 | 24.6 | 5.293 | 5.292 | 7216 | -16 | -40.8 | -24.3 |
| 45 per cent dioxane..... | 0-50 | 15.26 | 6.305 | 6.307 | 8600 | -394 | -43.3 | -30.2 |
| 70 per cent dioxane..... | 0-50 | 10.42 | 8.313 | 8.321 | 11347 | -594 | -44.6 | -40.1 |

* The results for boric acid have been fitted to equation 28 by making $p = 8 \times 10^{-8}$ instead of the value 5×10^{-8} , which was used for all of the other electrolytes in this table.

although other reactions (e.g., acetic acid) would be suitable. Subtracting the above three reactions in turn from the water reaction, and including the first of them, we obtain



Although the deviations from these average values amount to several calories, this classification is surprisingly clear-cut. Consideration of these reactions leads to several important conclusions.

ΔC_p^0 is more closely associated with the type of the reaction than the other thermodynamic quantities ΔF^0 , ${}^1\Delta H^0$, or ΔS^0 . The isoelectric reaction (b) produces practically no change in heat capacity, whereas reaction (a), which forms ions from neutral molecules, produces the greatest change in heat capacity. Reactions (c) and (d) are of the same *electrical* type but give rise to ΔC_p^0 of quite different magnitudes. ΔC_p^0 for reaction (c) is only -5 calories and is, in this respect, similar to the isoelectric type (b), while ΔC_p^0 for reaction (d) is about midway between the isoelectric type and reaction (a), which forms ions from neutral molecules. Furthermore, by subtracting reaction (c) from reaction (d) we obtain a second isoelectric reaction,



with another characteristic value of ΔC_p^0 . *These considerations show very clearly that the chemical type, as well as the electrical type, of these reactions, is important in determining the magnitude of ΔC_p^0 .* It is also brought out by table 3 that ΔC_p^0 for the ionization of acetic acid in aqueous mixed solvents is very nearly the same as that found in pure water, although the dielectric constant has been varied from 78.5 to 17.7.

A theoretical treatment of ionization equilibria involving considerations of molecular dissociation (non-Coulombic forces) and Coulombic forces between the ions is beyond the scope of the present purely thermodynamic discussion, but several papers dealing with this subject should be briefly noted. Moelwyn-Hughes (56) has derived a "semi-empirical" equation for K from kinetic considerations, and Gurney (10) has proposed a theory to separate the non-Coulombic from the electrostatic force effects and has interpreted different types of ionic equilibria on this basis.

Pitzer (71) points out that ΔC_p^0 for most of the electrolytes in table 3 is of the order of -40 calories. If this value is assumed to apply to the

first ionization of all of the electrolytes at all temperatures, their ionization constants may be expressed by the equation

$$\log K = A + B/T - 20 \log T \quad (35)$$

which has the orthodox form of equations 33 and 34 simplified by the assumption regarding ΔC_p^0 . He shows that this equation will express the data of table 1 over a wider temperature range than equation 28 and include the data for water as well. This gain in range, however, is obtained at considerable sacrifice in simplicity and ease of calculation, as the two adjustable parameters A and B must be obtained to a relatively large number of significant figures (cf. equations 33 and 34) if $\log K$ is to be reproduced within the experimental error. Within the temperature limits given in the second column of table 3 both equations are as good as the experimental data, but equation 28 is to be preferred because of its "slide-rule" convenience.

Pitzer also estimates from theoretical considerations that the entropy of ionization (first hydrogen only) of an acid should be of the order of -22 calories. The agreement of this figure with the average of the results in table 3 is surprisingly good, even in mixed solvents.

7. MIXED SOLVENTS. MEDIUM EFFECT

In discussing the influence of the solvent medium upon the numerical value of the activity coefficient, or ionization constant, of an ionized solute, reference will frequently be made to various medium effects. In a solution of an electrolyte in the presence of neutral (non-aqueous) molecules, the *total medium effect* is defined as the logarithm of the ratio of the activity coefficient of the electrolyte in the presence of the neutral molecules and in pure water at the same concentration of electrolyte. Both of the activity coefficients in this ratio are referred to unity at infinite dilution in pure water. The *primary medium effect* is the limit to which the total effect converges as the electrolyte concentration approaches zero. The *secondary medium effect* is always given by the difference between the total and primary effects.

To make use of these terms without confusion, we must be able to identify the reference state of any activity coefficient. Throughout this section all activity coefficients in any medium are understood to be referred to unity at infinite dilution in pure water unless written with an asterisk (*viz.*, γ^*), in which case they are referred to infinite dilution in the medium in which the solute is dissolved. When this medium is pure water, a superscript zero will be used (*viz.*, γ^0 , D^0 , etc.). A subscript zero indicates that the concentration of electrolyte is zero, except in the conventional

representation of standard potentials such as E_0 . Thus for all concentrations, we may write

$$\log \gamma = \log \gamma_0 + \log \gamma^* \quad (36)$$

or

$$\log \frac{\gamma}{\gamma^0} = \log \gamma_0 + \log \frac{\gamma^*}{\gamma^0} \quad (37)$$

since $\gamma_0^0 = 1$. This last equation gives the definitional relationship between the total, primary, and secondary medium effects (64) (appearing in that order from left to right).

Born (6) derived the equation

$$\log \gamma_0 = \frac{121}{r} \left(\frac{1}{D} - \frac{1}{D^0} \right) \quad (38)$$

for the primary medium effect on a uni-univalent electrolyte at 25°C. The effective radius, r , of the ions is defined by $2/r = 1/r_+ + 1/r_-$. Because of the oversimplified physical conditions subsumed in its derivation, this equation is only a rough approximation (65) at best. In mixed solvents in which a change in dielectric constant, D , is accompanied by a large change in the effective molecular weight of the solvent, the observed values of $\log \gamma_0$ may be much smaller than required by equation 38 and may even assume negative values in some cases (65).

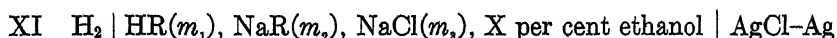
In very dilute solutions the secondary medium effect is given by

$$-\log \frac{\gamma^*}{\gamma^0} = 352 \left\{ \left(\frac{1}{D} \right)^{3/2} - \left(\frac{1}{D^0} \right)^{3/2} \right\} \sqrt{m} \quad (39)$$

for a uni-univalent electrolyte at 25°C. This equation is, of course, a consequence of the Debye-Hückel limiting law (8) and is a satisfactory expression for the influence of the solvent upon ion-ion interaction at low ionic strengths.

Very few studies of medium effect come within the scope of the title of this review, but they will suffice for purposes of illustration. The primary and total medium effects of undissociated acetic acid molecules upon hydrochloric acid have been directly measured (64) at 25°C., and it has been shown how these quantities may be taken into account in determining the ionization constants of weak electrolytes (35, 41). The primary medium effect of 10 and 20 per cent methanol (30) and of 20, 45, and 70 per cent dioxane (39) on acetic acid has been measured over a wide temperature range.

For simplicity the latter results will be considered first. The cells employed are represented by the following example:



There are two simple thermodynamically equivalent ways of expressing the electromotive force of such a cell, *viz.*,

$$\frac{F(E - E_0)}{2.3RT} = -\log m_{\text{H}} m_{\text{Cl}} - \log \gamma_{\text{H}} \gamma_{\text{Cl}} \quad (40)$$

and

$$\frac{F(E - E_0^*)}{2.3RT} = -\log m_{\text{H}} m_{\text{Cl}} - \log \gamma_{\text{H}}^* \gamma_{\text{Cl}}^* \quad (41)$$

In the first expression $-E_0$ is the standard potential of the silver-silver chloride electrode in pure water. In the second expression $-E_0^*$ is the standard potential in the mixed solvent. Combination of these two equations and comparison with equation 36 show that the primary medium effect of the alcohol upon the hydrogen and chloride ions is directly given by the two standard potentials. Thus

$$\log \gamma_{\text{HCl}} = \frac{1}{2} \log \frac{\gamma_{\text{H}} \gamma_{\text{Cl}}}{\gamma_{\text{H}}^* \gamma_{\text{Cl}}^*} = \frac{F(E_0 - E_0^*)}{4.6RT} \quad (42)$$

The primary medium effect of alcohol upon the activity coefficient, or ionization constant, of acetic acid can be determined by extrapolation of the data for the above cell in accordance with the procedure outlined in the fourth section of this review. Employing equation 41 we would obtain a quantity K_A^* the value of which is a function of the medium, because γ^* is always unity at infinite dilution. If we write

$$\gamma_A^2 = \frac{\gamma_{\text{H}} \gamma_{\text{R}}}{\gamma_{\text{HR}}} \quad \text{and} \quad k_A = \frac{m_{\text{H}} m_{\text{R}}}{m_{\text{HR}}}$$

the thermodynamic ionization constant in pure water, K_A , is related by the definitional equation,

$$K_A = \gamma_A^2 k_A = \gamma_0^2 \gamma_A^{*2} k_A = \gamma_0^2 K_A^* \quad (43)$$

to the properties of the acid in the mixed solvent. Accordingly,

$$\log \gamma_{0A} = \frac{1}{2} \log \frac{K_A}{K_A^*} \quad (44)$$

Table 4 contains the values of E_0^* and K_0^* obtained in methanol-water and dioxane-water mixtures and the corresponding values of $\log \gamma_{\text{HCl}}$ and $\log \gamma_{0A}$. The medium effect of acetic acid molecules upon hydrochloric

acid was calculated from the measurements of Owen.² It will be noticed that the medium effect of acetic acid upon hydrochloric acid is greater than that of methanol or dioxane and that the effects of the latter upon acetic acid are greater than upon hydrochloric acid. The medium effect of acetic acid molecules upon ionized acetic acid has not yet been determined experimentally, but it will be referred to in the discussion to follow.

If equation 40 were employed for extrapolation instead of equation 41, the situation would be similar, in some respects, to that encountered with cells containing unbuffered solutions of weak acids. The extrapolation equation can be written

$$\left[\frac{F(E - E_0)}{2.3RT} + \log \frac{m_R}{m_{HR}} m_{Cl} \right] = -\log K_A + 2 \log \gamma_A - 2 \log \gamma_{HCl} \quad (45)$$

TABLE 4
Results in various solvents at 25°C.

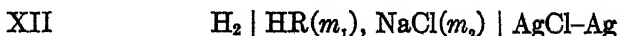
| SOLVENT | E_0^* | $10^3 \times K_A^*$ | $\log \gamma_{HCl}$ | $\log \gamma_A$ |
|----------------------------|---------------|---------------------|---------------------|-----------------|
| Pure water..... | 0.22239 (26)† | 1754 (25)† | 0.0 | 0.0 |
| 10 per cent methanol.... | 0.21535 (47) | 1247 (30) | 0.0595 | 0.0741 |
| 20 per cent methanol.... | 0.20881 (47) | 833 (30) | 0.1148 | 0.1614 |
| 20 per cent dioxane..... | 0.20303 (17) | 511 (19) | 0.1636 | 0.2678 |
| 45 per cent dioxane..... | 0.16352 (23) | 49.3 (19) | 0.4976 | 0.7755 |
| 70 per cent dioxane..... | 0.06395 (20) | 0.478 (19) | 1.3392 | 1.7823 |
| 82 per cent dioxane..... | -0.0415 (48) | 0.0072† | 2.230 | 2.69 |
| 10 per cent acetic acid... | 0.21050 (64) | | 0.1005 | |
| 20 per cent acetic acid... | 0.19682 (64) | | 0.2161 | |
| 30 per cent acetic acid... | 0.18091 (64) | | 0.3506 | |
| 40 per cent acetic acid... | 0.16211 (64) | | 0.5095 | |
| 50 per cent acetic acid... | 0.13945 (64) | | 0.7010 | |
| 60 per cent acetic acid... | 0.11150 (64) | | 0.9373 | |

† Reference to literature.

‡ Preliminary value obtained in this laboratory by Dr. Leslie D. Fallon.

Extrapolation of the left-hand member to zero ionic strength yields $-\log K_A + 2 \log \gamma_A - 2 \log \gamma_{HCl}$, so that, knowing K_A , we obtain the difference between the primary medium effect of methanol upon the weak acid and hydrochloric acid. From this it is clear that $\log \gamma_A$ cannot be obtained from the above cell unless either $\log \gamma_{HCl}$ or E_0^* is known (cf. equation 42).

We are now in a position to consider unbuffered cells of the type



* The relation employed is

$$(0.22239 - E_0^*)/0.059155 = \log \gamma_{HCl} = 5.87N/2 + \log d/d_0$$

which may be derived from equations 14 and 18 of reference 64.

first used to determine ionization constants (41) and the activity coefficients (43) of weak electrolytes in salt solutions. In such cells the weak acid concentration was maintained constant at some particular value of m_1 , while the salt concentration, m_2 , was varied. If the electromotive force expression for this cell be rearranged and $2 \log \gamma_{\text{HCl}}$ added to both sides of the equation, we can write

$$\left[\frac{F(E - E_0)}{2.3RT} + \log m_2 + 2 \log \gamma_{\text{HCl}} \right] = -\log m_{\text{H}} - 2 \log \frac{\gamma_{\text{HCl}}}{\gamma_{\text{HCl}}} \quad (46)$$

The right-hand member contains the total medium effect of the weak acid upon the chloride and hydrogen ions. This quantity is ordinarily unknown. We will therefore define an *apparent* hydrogen-ion concentration, m'_{H} , given by

$$\log m'_{\text{H}} = \log m_{\text{H}} + 2 \log \frac{\gamma_{\text{HCl}}}{\gamma_{\text{HCl}}} \quad (47)$$

and hence directly calculable from the left-hand member of equation 46. The corresponding apparent activity coefficient of the weak acid is defined in terms of the thermodynamic ionization constant by the equation

$$K_{\text{A}} = \frac{\gamma'_{\text{H}} \gamma'_{\text{R}}}{\gamma'_{\text{HR}}} \frac{m'^2_{\text{H}}}{m_1 - m'_{\text{H}}} = \gamma'^2_{\text{A}} k'_{\text{A}} \quad (48)$$

analogous to the expression

$$K_{\text{A}} = \frac{\gamma_{\text{H}} \gamma_{\text{R}}}{\gamma_{\text{HR}}} \frac{m^2_{\text{H}}}{m_1 - m_{\text{H}}} = \gamma^2_{\text{A}} k_{\text{A}} \quad (49)$$

connecting the real activity coefficient with the real hydrogen-ion concentration. In both of these expressions all activity coefficients are referred to unity at infinite dilution in pure water.

Combining equations 47, 48, and 49, we find that

$$\log \gamma'_{\text{A}} = \log \gamma_{\text{A}} - 2 \log \frac{\gamma_{\text{HCl}}}{\gamma_{\text{HCl}}} + \frac{1}{2} \log \frac{m_1 - m'_{\text{H}}}{m_1 - m_{\text{H}}} \quad (50)$$

which shows that $\log \gamma'_{\text{A}}$ is expressed in terms of real activity coefficients and indeed must simulate the properties of a real activity coefficient when the term containing m'_{H} is small. If the concentration, m_1 , of the weak acid is kept constant while the ionic strength is altered by variations in salt concentration, m_2 , we can obtain a series of values of m'_{H} and k'_{A} in a $m_1 - m_{\text{H}}$ molal solution of unionized weak electrolyte in water. So long as m_{H} is much smaller than m_1 , the composition of the solvent is very nearly constant, and the primary medium effect and, as a first approxi-

mation, the total medium effect may be considered independent of the salt concentration. It is therefore practicable to obtain

$$k'_{0A} = \lim_{\mu \rightarrow 0} k'_A$$

by extrapolation. The logarithm of the corresponding quantity

$$\gamma'_{0A} = \lim_{\mu \rightarrow 0} \gamma'_A$$

is of the nature of a primary medium effect, since it would be

$$\log \gamma_{0A} - 2 \log \gamma_{0\text{HCl}}$$

by equation 50 if the concentration term is eliminated by the extrapolation.

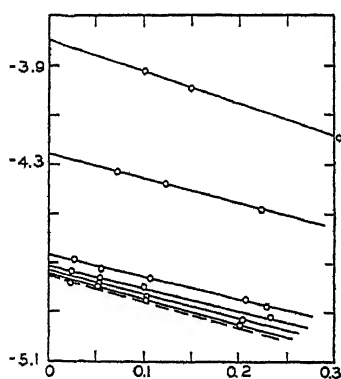


FIG. 7

FIG. 7. Evaluation of k'_{0A} for acetic acid at 25°C. for various values of m_1 . Reading down, $m_1 = 10.2, 5.41, 1.0, 0.52, 0.2$, and 0.1 . The dashed line represents the hypothetical limiting curve when $m_1 = 0$.

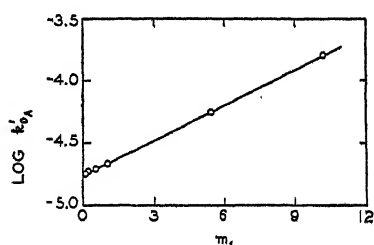


FIG. 8

FIG. 8. Evaluation of $\log K_A$ for acetic acid at 25°C.

The extrapolation of $\log k'_A$ is performed by means of the equations

$$\log k'_A - 2S\sqrt{\mu'} = \log k'_{0A} \pm 2\beta\mu' \quad (51)$$

or

$$\log k'_A - \frac{2S\sqrt{\mu'}}{1 + A\sqrt{\mu'}} = \log k'_{0A} \pm 2\beta\mu' \quad (52)$$

in which $\mu' = m_2 + m'_H$ is used for $m_2 + m_H$ as a very close approximation. The use of the numerical value of S for pure water neglects the secondary medium effect of the weak acid, but this approximation is unavoidable because the influence of HR molecules upon the dielectric constant of the solvent is generally unknown. The extrapolation is illustrated by figure 7,

in which $\log k'_{0A}$ is determined for acetic acid (41) for six values of m_1 by equation 51. A recent investigation (35) shows that it is necessary to use equation 52 if higher values of μ' are included.

From the nature of γ'_{0A} it is clear that it must become unity when $m_1 = 0$, for under this condition the medium is pure water. According to equation 48, extrapolation of k'_{0A} to $m_1 = 0$ must therefore yield K_A . This second extrapolation is shown in figure 8. The fact that this extrapolation is linear within the experimental error is without theoretical significance, as it is impossible at present to evaluate the effects of the several approximations involved in the calculations. It is known that $\log \gamma_{\text{HCl}}$ is not linear (64) when similarly plotted, but the behavior of $\log \gamma_A$ is unknown.³

The nearly parallel nature of the lines for low concentrations in figure 7 suggests that the broken line drawn from the intercept $\log K_A$ would closely represent the properties of infinitely dilute acetic acid in sodium chloride solutions. On such solutions the medium effect of the weak acid is zero. Therefore, dropping the primes in equation 51 or 52 and referring to equation 49, it follows that the slope of the broken line can be identified with 2β in an equation such as

$$2 \log \gamma_A = \log K - \log k_A = \frac{-2S\sqrt{\mu}}{1 + A\sqrt{\mu}} + 2\beta \quad (53)$$

which readily permits evaluation of the ionization, or activity coefficient, γ_A , of the weak acid in salt solutions.

Harned and Hickey (35) have determined k_A for acetic acid in sodium chloride solutions by this method from 0° to 40°C. They found that the temperature variation could be expressed by the relation

$$\log k_A = \log k_\theta - 5 \times 10^{-5}(t - \theta)^2 \quad (54)$$

similar to equation 28. This leads to the interesting conclusion that $\log \gamma_A$ varies linearly with temperature, for by combining equations 53 and 54 with equation 28 we can obtain

$$\log \gamma_A = 1/2 \log K_\theta/k_\theta + 2.5 \times 10^{-5}(\theta^2 - t^2) - 5 \times 10^{-5}(\theta - t)t \quad (55)$$

³ Owing to an unfortunate oversight in the paper of Harned and Owen (41), the third equality in their equation 17 is invalid, as it neglects the medium effect of acetic acid upon the real γ_A . The third sentence on page 5081 of that paper is also erroneous, as it refers γ_A to "a given solvent" rather than to pure water. These errors were not detected when Owen (64) correctly measured $\log \gamma_{\text{HCl}}$ directly and compared it with the value estimated from equation 17 of reference 47 and the slope of figure 8 of the present review. Although this "comparison" does not serve its original purpose, it might be taken to indicate that the medium effect on γ_A is smaller than that upon γ_{HCl} . It should be noted that the ordinate of figure 4 (reference 64) should have been labelled "2 log γ_θ ", as may be seen from the context.

Values of $\log k_0$ and ϑ are given in table 5. The average deviations between observed values of $\log k_A$ and those calculated by equation 54 are indicated by $\Delta_{ave.}$.

The behavior of the activity coefficients of two weak electrolytes in sodium chloride solutions is illustrated in figure 9, where they are compared with the activity coefficient of the strong electrolyte, hydrochloric acid, in the same salt solutions. Although the activity coefficients of

TABLE 5
Parameters of equation 54 for acetic acid in sodium chloride solutions

| μ | $-\log k_0$ | ϑ | $\Delta_{ave.}$ |
|-------|-------------|-------------|-----------------|
| 0.00 | 4.7544 | 22.6 | 0.0009 |
| 0.02 | 4.6388 | 25.1 | 0.0007 |
| 0.03 | 4.6189 | 25.6 | 0.0007 |
| 0.06 | 4.5798 | 26.4 | 0.0007 |
| 0.11 | 4.5432 | 27.6 | 0.0009 |
| 0.21 | 4.5061 | 29.2 | 0.0011 |
| 0.51 | 4.4752 | 32.3 | 0.0009 |
| 1.01 | 4.4957 | 35.7 | 0.0012 |
| 2.01 | 4.5875 | 45.0 | 0.0029 |
| 3.01 | 4.7132 | 50.9 | 0.0038 |

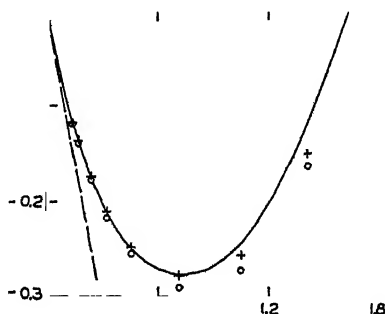


FIG. 9. Comparison of the activity coefficients of electrolytes in sodium chloride solutions at 25°C. Smooth curve, $\log \gamma_H \gamma_{Cl}$; O, $\log \gamma_H \gamma_{OH}/a_{H_2O}$; +, $\log \gamma_H \gamma_{Ac}/\gamma_{HAc}$.

other weak acids and ampholytes have been studied by means of cells without liquid junctions, they are not included in figure 9, because the corrections for medium effects were incomplete or neglected. A large number of such systems have also been studied by cells with liquid junctions (50, 51, 52), and by catalytic (7, 34) or optical (11, 12, 13) methods.

The simplest interpretation of the close similarity in the behavior of $\log \gamma_H \gamma_{Cl}$ and $\log \gamma_H \gamma_{Ac}/\gamma_{HAc}$, or $\log \gamma_H \gamma_{OH}/a_{H_2O}$, is to infer that the effect of the ionic strength of the salt upon the two terms γ_{HAc} and a_{H_2O} is relatively

insignificant in dilute solutions. The correctness of this inference is born out by theory and by a considerable body of experimental evidence. Using an optical method, von Halban, Kortüm, and Seiler (13) have very accurately separated the activity coefficient function for the weak acid α -dinitrophenol into γ_{\pm} , for the ionic constituents, and γ_u for the undissociated neutral molecule. They found $\log \gamma_u$ approximately linear in μ . More recently (49) cells without liquid junctions have been used to yield such information. Larson and Tomsicek (49) found that γ_{HAc} in a 0.5 normal acetic solution was changed less than 10 per cent when the ionic strength was increased to unity by addition of potassium acetate.

By combination of the activity coefficients derived for acetic acid (35) with values (40) of $\gamma_w = \gamma_{\text{H}}\gamma_{\text{OH}}/a_{\text{H}_2\text{O}}$, the influence of sodium chloride upon

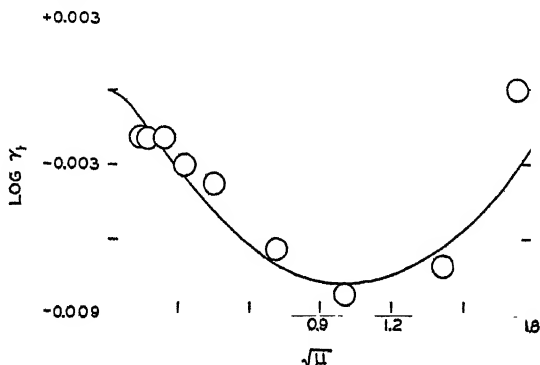
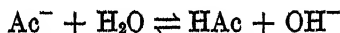


FIG. 10. Variation of $\log \gamma_h$ for hydrolysis of acetate ion in sodium chloride solutions at 25°C.

the hydrolysis of the acetate ion (at infinite dilution) can be readily investigated. The relationship between the hydrolytic reaction,



and the ionization reactions of water and acetic acid is

$$K_h = \frac{K_w}{K_A} = \frac{\gamma_{\text{HAc}}\gamma_{\text{OH}}}{a_{\text{H}_2\text{O}}\gamma_{\text{Ac}}} \frac{m_{\text{HAc}}m_{\text{OH}}}{m_{\text{Ac}}} = \frac{\gamma_w^2}{\gamma_A^2} \frac{k_w}{k_A} = \gamma_h^2 k_h \quad (56)$$

Since the four quantities γ_w , k_w , γ_A , and k_A are separately known in sodium chloride solutions, γ_h and k_h can be evaluated in these solutions. Values of γ_h can be calculated from K_h and k_h tabulated by Harned and Hickey (36, 37). The results at 25°C. are plotted in figure 10 as circles, the radii of which represent an uncertainty of 0.1 per cent in γ_h .

Figure 10 brings out two interesting points. The total variation of γ_h with salt concentration is very small, being less than 2 per cent. This nearly ideal behavior of the hydrolysis reaction maintains also at 30° and

40°C., but tends to disappear at lower temperatures. The second point of interest is the form taken by the plot in dilute solutions. Since γ_h is $\gamma_{\text{HAc}}\gamma_{\text{OH}}/a_{\text{H}_2\text{O}}\gamma_{\text{Ac}}$ by equation 56, a plot of $\log \gamma_h$ against $\sqrt{\mu}$ must approach the intercept, $\log \gamma_h = 0$, with zero slope. It is clear from the figure that this condition is not fulfilled at the lowest experimental concentration, 0.02 *M*. To illustrate the extreme dilutions which might be required before the plot shows definite signs of becoming horizontal, the curve is drawn for the ratio of two hypothetical univalent ions conforming to the Debye-Hückel equation. The "*a*" values were taken as 4.0 and 4.5 Å., and a linear term, 0.005 μ , was selected to give approximate agreement with the data at high ionic strengths. The numerical values of these parameters are too arbitrary to be significant individually, but they demonstrate the essential conformity of the data with modern theory, and their difference, 0.5 Å., calls attention to the very small magnitude of the effect which has been measured experimentally.

8. SUMMARY⁴

1. A careful analysis is made of the methods by which the thermodynamic properties of weak electrolytes may be determined in water, in salt solutions, and in mixed solvents by means of cells without liquid junctions. It is shown that thermodynamic ionization constants can be exactly determined by suitable cell measurements, but that the accuracy with which the concentrations of the ions of a weak electrolyte (water) in salt solutions can be determined is limited to the accuracy with which we know the degree of ionization of certain strong electrolytes.

2. Two methods for determining the thermodynamic ionization constant of water are described and illustrated.

3. It is shown how the ionization product, $m_{\text{H}}m_{\text{OH}}$, can be evaluated in neutral salt solutions.

4-5. Suitable cells for determining the thermodynamic ionization constants of weak acids, bases, and ampholytes are described in detail. The practical graphical methods employed in the calculations are illustrated by five examples.

6. Numerical values of the ionization constants are tabulated for all of the weak electrolytes, of various types, investigated by these methods. These results are compared with values obtained by conductometric methods and by cells with liquid junctions.

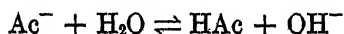
With the exception of the values for water and the hydrosulfate ion, these ionization constants may be expressed by the equation

$$\log K = \log K_0 - p(t - \theta)^2$$

⁴ The numbering of the paragraphs in the summary is identical with that of the corresponding section headings of this review.

over a 30° to 50°C. temperature interval within the apparent experimental errors. The constant p has the value 5×10^{-5} , except in the case of boric acid, where 8×10^{-5} is used. By means of this equation, ΔF^0 , ΔH^0 , ΔS^0 , and ΔC_p^0 for the ionization reactions at unit activities have been estimated and their values at 25°C. tabulated. It is remarked that ΔC_p^0 is more simply associated with the type of the ionization reaction than the other thermodynamic functions, and certain generalizations of a qualitative nature are pointed out.

7. The formal influence of variations in the solvent medium upon the thermodynamic properties of the solute is presented. By separating this influence into a primary and secondary medium effect, it is shown what quantities may be determined from cell measurements involving mixed solvents. In the light of this information, the interpretation of cell measurements on unbuffered weak acids in salt solutions is treated in some detail. It is shown how the activity coefficients of weak electrolytes may be estimated in neutral salt solutions. The hydrolytic reaction,



is discussed, and some of the thermodynamic properties of this equilibrium are illustrated.

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SMOKE-FORMING CHEMICALS

KIRBY E. JACKSON¹

Department of Chemistry, Georgia School of Technology, Atlanta, Georgia

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According to Prentiss (261) the colloidal state of matter is characterized by an intimate admixture of at least two phases,—the dispersed phase and the dispersion medium. By a dispersion of this kind is meant the regular distribution of one substance in another in such a way that the individual particles of the one substance are suspended separately from each other in the second substance. In this sense smoke is to be regarded as a two-phase colloid whose dispersion medium (the air) is in the gaseous state and whose dispersed phase is a solid or liquid. So-called colloidal solutions of this kind have physical and chemical behavior entirely different from that of normal solutions, in that the size of the particles may vary within certain limits without causing the solution to lose its colloidal character.

The particles of a smoke or fog vary in size from those just large enough to be perceived by the unaided eye to those that approach the size of a single molecule. In general, smoke particles are intermediate in size between dust particles (10^{-4} cm.) and gas particles (10^{-7} cm.) and average about 10^{-5} cm. in diameter. As a rule, the smaller the particles in a given quantity of smoke, the greater is their obscuring power; hence the aim is to generate a smoke consisting of the maximum number of particles of medium size.

Since smoke is a suspension of minute solid or liquid particles, it is not a true gas and does not follow the law of gaseous diffusion. However, owing to the collisions of the molecules of air with the smoke particles, the latter exhibit Brownian movements, as a result of which they gradually diffuse and spread. Because of their greater mass and inertia and the resistance of the air, the larger particles of smoke diffuse more slowly than the smaller ones. But, compared with the effects of wind and convection currents, diffusion plays an almost negligible part in the dispersion of smokes; even in a very dense smoke the weight of the smoke particles is only a small fraction of 1 per cent of the weight of the air it occupies, so that a smoke cloud is distinguished from the surrounding atmosphere only by the small amount of suspended foreign material.

¹ Present address: 2514 Belmont Boulevard, Nashville, Tennessee.

If smoke is released in warm air, it will rise as the warm air expands. If released in cold air, where these upward convection currents are absent, the smoke will spread out in a horizontal layer and cling to the ground. The movement of the cloud is therefore merely the movement of the air, which accounts for the characteristic behavior of smoke clouds.

Since floating smoke particles are themselves heavier than air, they gradually fall, although at a very slow rate which varies with the size of the particles. Thus, according to Grey and Patterson (120), a smoke particle having a diameter of 10^{-4} cm. falls about 0.071 in. per minute, which is so slow as to be negligible for practical purposes.

In the same manner as particles in colloidal solution, smoke particles tend to unite and increase in size by cohesion and coalescence as they come in contact with each other by Brownian movements or air currents. This agglomeration takes place much more rapidly in a dense than in a thin smoke. When the smoke particles are completely dry, agglomeration is not observed, but when the particles are liquid, or of a deliquescent solid with condensed surface moisture, this is more pronounced. The increase in the number and size of the larger at the expense of the smaller particles increases the rate of settling and decreases the concentration of the cloud. Also, the smaller smoke particles vaporize more rapidly because their surfaces are greater in proportion to their weight. Thus it follows that a smoke is most stable when the particles are of the minimum size and consist of a dry non-deliquescent solid material.

Fries and West (101) classify smokes as screening and toxic: included among the former are phosphorus, chlorosulfonic acid, oleum, sulfur trioxide, tin tetrachloride, silicon tetrachloride, and titanium tetrachloride; among the latter are methyldichloroarsine (154), phenyldichloroarsine, diphenylcyanoarsine (155), triphenylchloroarsine, diphenylchloroarsine (156), and cyanogen bromide. The smoke-forming chemicals described in this article are phenyldichloroarsine, chlorosulfonic acid, titanium tetrachloride, and silicon tetrachloride.

I. PHENYLDICHLOROARSINE, $C_6H_5AsCl_2$

Preparation

Michaelis (209) in 1875 first prepared phenyldichloroarsine by heating mercury diphenyl with excess arsenious chloride at $170^\circ C$. Since that time many modifications and new processes have been devised, as illustrated by the following methods of preparation: by warming phenylarsenious oxide with hydrochloric acid (180, 211); by passing a mixture of arsenic trichloride and benzene through a tube heated to redness (180) or by heating it for 40 hr. (179); by the decomposition of phenyltetrachloroarsine with glacial acetic acid (180); by the decomposition of diphenyl-

chloroarsine (180); by heating diphenyltrichloroarsine in a sealed tube to 200°C. (180); by heating triphenylarsine with excess aluminum chloride under pressure to 250°C. (216); by the oxidation of phenylhydrazine with pyroarsenic acid, phenylarsenic acid, or arsenic acid in the presence of copper (372); by heating phenyl(β -ethylmercaptoethyl) arsinic acid or phenyl(β -ethylmercaptophenyl)arsinic acid with phosphorus trichloride (310); by the reduction of phenylarsenic acid (51); by the decomposition of 10-phenyl-9,10-dihydrophenarsazine (371) or of 10-phenyl-5,10-dihydrophenarsazine (2) with gaseous hydrogen chloride; by the action of thionyl chloride on phenylarsenic acid (321). By heating triphenylarsine for 3 hr. with arsenic trichloride at 250-280°C. Morgan and Vining (225) obtained phenyldichloroarsine from the fraction coming over between 150° and 190°C. Heating phenylmercuric chloride with arsenic trichloride (278), heating arsenic trichloride and benzene in the presence of aluminum chloride (172, 357) or calcium chloride, or heating phosphorus trichloride and benzene in the presence of arsenic trichloride (180) produces phenyldichloroarsine. When triphenylbismuthine (54) or triphenylstibine (53) in anhydrous ether is heated with arsenic trichloride, phenyldichloroarsine is obtained as one of the products. The reaction of triphenylarsine in anhydrous ether with antimony trichloride (53), or of triphenylbismuthine or triphenylarsine with arsenic trichloride (53), produces the chloroarsine. Phenylmethylchloroarsine, phenylmethylarsinic acid, diphenylarsinic acid, or diphenylarsenious chloride when treated with thionyl chloride (113) forms phenyldichloroarsine. Reduction of phenyl(*p*-thiocyanophenyl)arsinic acid in cold hydrochloric acid with sulfur dioxide (311) produces phenyldichloroarsine. A benzene solution of triphenylchloromethane treated with a benzene solution of phenylarsine forms phenyldichloroarsine (34). Upon heating phenylarsenic oxide with concentrated hydrochloric acid (322) phenyldichloroarsine results. When moist chlorine, cooled phosphorus pentachloride, chloral, or chloral hydrate is allowed to react with bis(α -hydroxyethyl)phenylarsine, phenyldichloroarsine is produced (245). It is also obtained by heating triphenylarsine with arsenic trichloride for 30 hr. at 250°C. (215) or by heating azobenzene with chlorine (218). By treating phenylchloroarsineacetic acid with a chloroform solution of phosphorus pentachloride, Quick and Adams (266) prepared phenyldichloroarsine; Sherlin and Yakubovich (310) obtained it by acidifying phenyl(β -ethylphenylmercapto)arsine chloride with hydrochloric acid. Oechsli (239) obtained British patent 173,796 (July 10, 1920) for the preparation of phenyldichloroarsine by heating a diarylarsine with arsenic trichloride; Pope and Turner (260) obtained British patent 142,880 (June 11, 1918) for the preparation of phenyldichloroarsine by heating triphenylarsine with arsenic trichloride for 4 hr. at 300°C.

Physical properties

Phenyldichloroarsine is a colorless, strongly refractive liquid of mildly unpleasant odor (209). It is not hydrolyzed or dissolved by water even on heating; however, it is easily dissolved by all alkalis (180).

Its boiling point has been reported as follows: 114°C. at 14 mm. (322); 117–120°C. at 7 mm. (371); 118°C. at 9 mm. (138); 124.5–125°C. at 12 mm. (126); 127°C. at 12 mm. (113); 127–130°C. at 10–11 mm. (310); 128°C. at 16 mm. (113); 153–155°C. at 18 mm. (245); the following boiling points have been found at atmospheric pressure: 249°C. (209); 250–252°C. (215); 250–255°C. (278); 252–253°C. (371); 252–255°C. (210); 254°C. (180, 212); 254.4–257.6°C. (126). The following values have been reported for the density: $d_4^{17.5^\circ}$, 1.655; $d_4^{39.5^\circ}$, 1.628; $d_4^{60.5^\circ}$, 1.601; $d_4^{79.5^\circ}$, 1.578 (138); $d_4^{19^\circ}$, 1.6516; $d_4^{15.3^\circ}$, 1.6561 (126); $d_4^{24^\circ}$ (vacuum), 1.646 (157). The molecular refraction for the D sodium line at 24°C. is 48.50 (157). Gryszkiewicz-Trochimowski and Sikorski (126) found the index of refraction at 15.3°C. to be as follows: $n_\alpha = 1.6313$; $n_D = 1.6386$; $n_\beta = 1.6575$. The values of the molecular refraction are 47.99 for the H_α line, 48.43 for the D line, and 49.56 for the H_β line.

Baxter, Bezzenberger, and Wilson (10) determined the vapor pressure of phenyldichloroarsine by the "air current" or "transference" method. A known volume of air, as determined by the measured volume of water run out of an aspirator, was saturated with the vapor of phenyldichloroarsine by passing it through a weighed receptacle maintained at constant temperature in a water thermostat. The loss in weight of the saturating tube furnished the weight of evaporated substance. From the latter quantity the volume of vapor was calculated on the assumption that the volume of a gram-molecule under standard conditions is 22.4 liters. The per cent of vapor multiplied by the interior pressure, as determined by the barometric reading and an open-arm manometer attached to the aspirator, gave the vapor pressure. The control of the temperature in the thermostat was within 0.1°C. A plot of the logarithm of the vapor pressure against the reciprocal of the absolute temperature gives a very nearly straight line, which, therefore, can be represented by an empirical equation of the form:

$$\log \text{vapor pressure} = A + B/273 + t$$

Vapor pressure values calculated by means of these equations agreed with the observed values within the experimental error (see table 1). For a higher degree of accuracy the equations were not adequate, however, and can not be trusted for extrapolation over any considerable range.

Henley and Sugden (138) calculated the parachor of phenyldichloroarsine by the formula:

$$[P] = M\gamma^{\frac{1}{3}}(D - d)$$

where M = molecular weight, γ = surface tension (dynes per centimeter) determined by the method of maximum bubble pressure, and D and d are the densities of liquid and vapor, respectively, which were determined by means of a U-shaped pyknometer (see table 2).

Blicke and Smith (36) determined the molecular weight of phenyldichloroarsine by the ebullioscopic procedure in the Menzies apparatus, using benzene as solvent: $(\Delta t^\circ) = 0.1968$; molecular weight found (A) = 234; molecular weight calculated (B) = 223; A/B = 1.05.

TABLE 1
Vapor pressure of phenyldichloroarsine
 $\log \text{vapor pressure} = 9.150 - 3164/273 + t$

| TEMPERATURE | VAPOR PRESSURE (OBSERVED) | VAPOR PRESSURE (CALCULATED) | DIFFERENCE (CALCULATED—OBSERVED) |
|-------------------|------------------------------|--------------------------------|-------------------------------------|
| $^\circ\text{C.}$ | <i>mm.</i> | <i>mm.</i> | <i>mm.</i> |
| 45 | 0.159 | 0.159 | 0.000 |
| 35 | 0.076 | 0.076 | 0.000 |
| 30 | 0.049 | 0.051 | +0.002 |
| 25 | 0.035 | 0.034 | -0.001 |
| 15 | 0.014 | 0.014 | 0.000 |
| 0 | 0.004 | 0.004 | 0.000 |

TABLE 2
Parachor of phenyldichloroarsine

| TEMPERATURE | γ | D | P |
|-------------------|----------|-------|-------|
| $^\circ\text{C.}$ | | | |
| 18.5 | 44.64 | 1.654 | 348.3 |
| 42.0 | 41.51 | 1.624 | 348.3 |
| 62.6 | 38.72 | 1.600 | 347.5 |
| 79.0 | 37.33 | 1.578 | 349.1 |
| Mean value..... | | | 348.3 |

Chemical properties

(1) *Heating.* When phenyldichloroarsine is passed through a red-hot tube, decomposition takes place, the products being diphenyl, arsenic trichloride, and arsenic (180).

(2) *Action with inorganic salts.* An absolute alcoholic solution of phenyldichloroarsine when shaken with sodium iodide forms phenyldiiodoarsine, $\text{C}_6\text{H}_5\text{AsI}_2$, lemon-yellow needles, m.p. 15°C. (49, 323) and b.p. 185°C. (323); this compound decomposes at 190°C. (49).

When phenyldichloroarsine is treated with silver cyanide there is formed

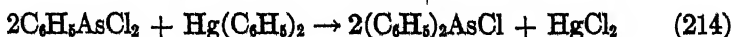
crystalline phenylarsinedicyanide, $C_6H_5As(CN)_2$, which melts at 78.5–79.5°C. and possesses a feeble aromatic odor (125).

(3) *Action with ammonia and alkalies.* When dry ammonia is passed into an anhydrous benzene solution of phenyldichloroarsine the reaction goes on smoothly with formation of phenylarsenimide, $C_6H_5As=NH$, which is easily soluble in benzene and xylene but difficultly soluble in ether and absolute alcohol. It separates as beautiful flakes from absolute alcohol (212). It begins to sinter at 265°C. and melts at 270°C. (212). The nitrogen is only feebly attached to the arsenic atom, hydrolysis being readily effected by moisture. The imide is very irritating to the skin in the powder form, in the vapor of a volatile solvent, and in solution (153).

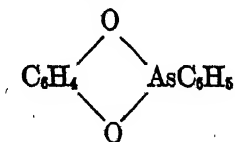
Upon boiling phenyldichloroarsine with concentrated sodium hydroxide solution (180), sodium carbonate (211), or sodium bicarbonate (49) there is formed phenylarsenious oxide, C_6H_5AsO . At ordinary temperatures it has an anise-like odor. On warming it attacks the mucous lining of the nose. It is insoluble in water, feebly soluble in cold alcohol, but easily soluble in hot alcohol and cold benzene. It melts at 119–120°C.

(4) *Action with mercury and lead compounds.* When mercury dibutyl and phenyldichloroarsine are allowed to react there is formed phenylbutylchloroarsine, $C_6H_5(C_4H_9)AsCl$, a clear yellow liquid, boiling at 165–166°C. at 14 mm. Its density at 0°C. is 1.35 (337).

Depending upon the relative amounts of mercury diphenyl and phenyldichloroarsine used, the following compounds are formed: triphenylarsine, $(C_6H_5)_3As$; diphenylchloroarsine, $(C_6H_5)_2AsCl$; phenylmercuric chloride, C_6H_5HgCl . This is illustrated by the following equations:



Through the action of phenyldichloroarsine on lead pyrocatechol there is formed pyrocatechol phenylarsenite,



as a white, radiant, crystalline mass; it melts at 83°C. and boils at 197–198°C. at 15 mm. In water it decomposes to phenylarsenious oxide and pyrocatechol (211).

(5) *Action with sodium salts.* Phenyldichloroarsine in 10 N sodium

hydroxide solution upon being brought in contact with an aqueous solution of sodium chloroacetate produces no immediate reaction, but within 30 min. the reaction is complete. After recrystallization from hot water the product, phenylarsenoacetic acid, $C_6H_5As(O_2H)CH_2COOH$, melts at $141-142^\circ C$. (with decomposition) (266).

An aqueous solution of sodium chloroacetoarsanilate is added to a solution of phenyldichloroarsine in 10 *N* sodium hydroxide. The chalky white material is extracted with hot water, then with hot alcohol, and finally dried at $110^\circ C$. The product, *p*-phenylarsinoacetoarsanilic acid, $C_6H_5As(O_2H)CH_2CONHC_6H_4AsO_3H_2$, does not melt below $250^\circ C$. (255).

A xylene solution of phenyldichloroarsine, reacting with a xylene solution of sodium benzoate, forms dibenzyl phenylarsenite, $C_6H_5As(OCH_2C_6H_5)_2$, a yellowish liquid having an odor like that of benzyl alcohol and boiling at $296^\circ C$. at 30 mm. Its specific gravity at $13^\circ C$. is 1.2853 (212).

When an aqueous solution of sodium *o*-chloroacetoaminobenzoate is added to phenyldichloroarsine in 10 *N* sodium hydroxide solution, the product is phenylarsino-*o*-acetoaminobenzoic acid, $C_6H_5As(O_2H)CH_2CONHC_6H_4COOH$ (*o*), m.p. $198-200^\circ C$. (with decomposition) (266).

Kharasch (166) obtained U. S. patent 1,589,599 (June 22, 1926) for the formation of the compound $C_6H_5As(SCH_2COOH)_2$, resulting from the action of an aqueous solution of a metal salt of thioglycolic acid on phenyldichloroarsine. This compound has germicidal and therapeutic properties.

(6) *Action with halogens and halogen compounds.* Upon direct addition of chlorine to phenyldichloroarsine, Dehn and Wilcox (74) and Michaelis (209, 210, 211) found that phenyltetrachloroarsine, $C_6H_5AsCl_4$, is formed in yellow needles, melting at $45^\circ C$. On addition of water to the tetrachloride the oxychloride, $C_6H_5AsOCl_2$, is formed; with more water phenylarsinic acid, $C_6H_5AsO(OH)_2$, is formed, which crystallizes very readily in long white needles, melting at $168^\circ C$.

p-Dibromobenzene results from the action of bromine on phenyldichloroarsine. It forms colorless monoclinic crystals, m.p. $89^\circ C$. (180, 211).

Schuster (307) found that when phenyldichloroarsine is boiled for 45 min. with fuming hydrogen bromide (density, 1.75) the yield of the bromine derivative by the replacement of the arsenic radical is not very good.

A mixture of phenyldichloroarsine, alcohol, sodium hydroxide, and methyl iodide after standing for one day was neutralized with hydrochloric acid; phenylmethyliodoarsine, $C_6H_5(CH_3)AsI$, was formed (50).

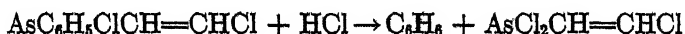
The reaction between phenyldichloroarsine in 10 *N* sodium hydroxide solution and ethylene bromide forms ethylenediphenyldiarsinic acid,

$C_2H_4(C_6H_5AsO_2H)_2$, which separates first as an oil but gradually solidifies, and upon recrystallization from hot water or alcohol melts at 209–211°C. (266).

Phenyldichloroarsine when treated with *p*-bromotoluene and finely sliced sodium in anhydrous ether forms white, rhombohedral crystals of phenylditolylarsine, $C_6H_5As(C_7H_7)_2$, m.p. 101°C. This compound is soluble in ether, chloroform, benzene, and hot alcohol, and slightly soluble in cold alcohol and glacial acetic acid (212).

Phenyldichloroarsine when treated with bromoxylene and finely divided sodium in anhydrous ether forms *m*-dixylylphenylarsine, $C_6H_5(C_6H_4(CH_3)_2)_2As$, as an oil which, on rubbing, separates as needles of the triclinic system, m.p. 99°C. This substance is soluble in most organic solvents but only slightly soluble in cold alcohol. It is refractive (213).

(7) *Action with hydrocarbons.* Hunt and Turner (147) found that acetylene is slowly absorbed by a solution of anhydrous aluminum chloride in phenyldichloroarsine to give, after treatment with ice and hydrochloric acid, phenyl- β -chlorovinylidichloroarsine, $AsC_6H_5ClCH=CHCl$, a pale yellow, unpleasant smelling liquid boiling at 140–145°C. at 10 mm., phenyl- $\beta\beta'$ -dichlorodivinyarsine, $AsC_6H_5(CH=CHCl)_2$, boiling at 155–160°C. at 10 mm., and compounds of higher boiling point. The last, which have not been investigated further, arise mainly from the intermolecular condensation of phenyldichloroarsine, a process which is preceded by the formation of a crystalline additive compound, $AsC_6H_5Cl_2 \cdot AlCl_3$. If the $C_6H_5AsCl_2 \cdot AlCl_3$ solution is not cooled during the absorption of acetylene, or if the ice-acid treatment is omitted, β -chlorovinylidichloroarsine and benzene are also formed, in accordance with equations of which the simplest is:



A solution of anhydrous aluminum chloride in cold phenyldichloroarsine on standing for a few hours deposits the additive compound, $AsC_6H_5Cl_2 \cdot AlCl_3$, as pale yellow crystals. If the additive compound, or a freshly prepared solution of aluminum chloride in the phenyldichloroarsine, is treated with hydrochloric acid, phenyldichloroarsine is recovered unchanged, but if the solution is kept for more than a few hours a mixture of products results, with boiling points ranging from 130°C. to 270°C. at 15 mm., being higher the longer the solution stands (147).

When phenyldichloroarsine is shaken with a mixture of aluminum chloride and cyclohexane for 16 hr. at 65–70°C., it is reduced with the formation of free arsenic (233).

(8) *Action with sodium derivatives of alcohols and phenols.* By the action

of an ethereal solution of phenyldichloroarsine on sodium methylate there is formed dimethyl phenylarsenite, $C_6H_5As(OCH_3)_2$, a colorless, characteristic smelling liquid, having a boiling point of $116^\circ C.$ at 18 mm. and $220^\circ C.$ at 760 mm. Its specific gravity at $20^\circ C.$ is 1.343. It hydrolyzes easily in water or alkali, forming phenylarsenious oxide and methyl alcohol (212).

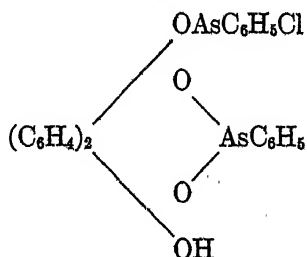
An ethereal solution of sodium ethylate acts upon phenyldichloroarsine to form diethyl phenylarsenite, $C_6H_5As(OC_2H_5)_2$, a colorless, unpleasant smelling liquid, boiling at $122^\circ C.$ at 15 mm. (212). McKenzie and Wood (191) found that when an alcoholic solution of sodium ethylate was added to phenyldichloroarsine, and the mixture was heated on a water bath and distilled under diminished pressure, phenylethoxychloroarsine, $C_6H_5AsClOC_2H_5$, was obtained. This is a colorless oil, boiling at $125-126^\circ C.$ at 12 mm. It gradually undergoes hydrolysis in contact with water, being transformed into a white solid which, when recrystallized from petroleum, separates in needles which melt at $127-130^\circ C.$ It is curious that this product has a melting point considerably higher than that recorded in the literature for phenylarsenious oxide.

An ethereal solution of sodium phenylate in contact with phenyldichloroarsine forms diphenyl phenylarsenite, $C_6H_5As(OC_6H_5)_2$, a colorless liquid, boiling at $245^\circ C.$ at 15 mm. Its specific gravity at $20^\circ C.$ is 1.32 (212).

A xylene solution of phenyldichloroarsine reacts with a xylene solution of sodium tolylate forming ditolyl phenylarsenite, $C_6H_5As(OC_6H_4CH_3)_2$, a yellowish oil boiling at $285^\circ C.$ at 12 mm. Its specific gravity at $13^\circ C.$ is 1.2989 (212).

By the reaction of the sodium derivative of β -naphthol in ether with an ethereal solution of phenyldichloroarsine there is formed di- β -naphthyl phenylarsenite, $C_6H_5As(OC_{10}H_7)_2$, in colorless needles melting at $113-114^\circ C.$ (212).

By the action of phenyldichloroarsine on sodium pyrocatecholate there is formed the chlorine-containing compound,



m.p. $63^\circ C.$ (212).

(9) *Action with sulfides.* When hydrogen sulfide is passed into an aqueous or alcoholic solution of phenyldichloroarsine there results phenylarsinosulfide, C_6H_5AsS , a yellowish white powder; its melting point has been reported as $152^\circ C$. (177, 230, 304) and as 174 – $176^\circ C$. (36).

Upon treating the sodium salt resulting from the action of phenyldichloroarsine and sodium hydroxide with ethyl β -bromoethyl sulfide and oxidizing the resulting product, there is formed phenyl(β -ethylmercaptoethyl)arsinic acid, $C_6H_5As(O_2H)C_2H_4SC_2H_5$, as colorless needles or six-sided prisms, melting at $177^\circ C$. It is soluble in alcohol, acetone, carbon disulfide, and hot water, and insoluble in hydrochloric acid (310).

Phenyl(β -ethyl isoamylsulfone)arsinic acid, $C_6H_5As(O_2H)C_2H_4SO_2C_6H_{11}$, results from treating the sodium salt formed from phenyldichloroarsine and sodium hydroxide with isoamyl β -bromoethyl sulfide and oxidizing the product. It forms long colorless crystals, melting at 139.5 – $140.5^\circ C$. It is slightly soluble in hot water and acetone (310).

Phenyl(β -phenylsulfonyl ethyl)arsinic acid, $C_6H_5As(O_2H)C_2H_4SO_2C_6H_5$, results from treating the sodium salt formed from phenyldichloroarsine and sodium hydroxide with phenyl β -bromoethyl sulfide and oxidizing the product. It is obtained as long needles, melting at 192 – $193^\circ C$. (with slight decomposition) (310).

(10) *Action with zinc alkyls.* Dimethylphenarsazine, $(CH_3)_2C_6H_5As$, b.p. $200^\circ C$., is formed as the result of the reaction between zinc methyl and phenyldichloroarsine (214).

A dilute benzene or ether solution of phenyldichloroarsine added dropwise to zinc ethyl forms a colorless, highly refractive liquid of unpleasant odor, diethylphenarsazine, $(C_2H_5)_2C_6H_5As$, boiling at $240^\circ C$. (180, 211, 364).

(11) *Action with Grignard reagents.* Upon treating magnesium shavings in ether with methyl bromide and adding phenyldichloroarsine there is formed dimethylphenarsazine, $(CH_3)_2C_6H_5As$, b.p. 193 – $200^\circ C$. (323).

Phenyldichloroarsine by reacting with methylmagnesium iodide forms phenyldimethylarsine, $C_6H_5(CH_3)_2As$, b.p. $200^\circ C$. (364). Henley and Turner (139) obtained phenyltrimethylarsonium thiophenoxide by treating phenyldichloroarsine with methylmagnesium iodide. It melts at 144 – $145^\circ C$. It crystallizes from alcohol-ether solution in white leaflets, soluble in water or alcohol but insoluble in ether.

A Grignard reagent prepared from ethyl bromide, magnesium, and ether was treated gradually with a benzene solution of phenyldichloroarsine. After appropriate treatment there was obtained phenyldiethylarsine, $C_6H_5(C_2H_5)_2As$, a colorless oil, boiling at 111 – $115^\circ C$. at 14 mm. (49).

Phenyldichloroarsine reacts with *n*-propylmagnesium bromide to give

phenyldipropylarsine, $\text{C}_6\text{H}_5(\text{C}_3\text{H}_7)_2\text{As}$, which boils at 125°C . at 10 mm. and at 141°C . at 19 mm. Other physical constants are: d_4^{20} , 1.1078; n_D^{20} , 1.5595; n_D^{20} , 1.59631; n_C^{20} , 1.5409 (159).

Phenyldichloroarsine reacts with *n*-amylmagnesium bromide to give phenyldiamylarsine, $\text{C}_6\text{H}_5(\text{C}_5\text{H}_{11})_2\text{As}$, which boils at 174°C . at 10 mm., and at 186°C . at 16 mm. (159).

Phenyldichloroarsine reacts with cyclohexylmagnesium bromide to form dicyclohexylphenylarsine, $(\text{C}_6\text{H}_{11})_2\text{C}_6\text{H}_5\text{As}$, a colorless liquid, boiling at 220°C . at 14 mm. (276, 319).

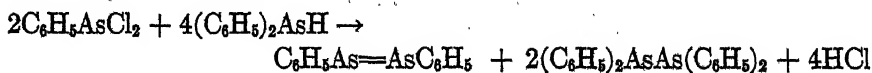
When the magnesium compound from 1,4-dibromobutane reacts with phenyldichloroarsine there is obtained cyclotetramethylenephénylarsine, $(\text{CH}_2)_4\text{AsC}_6\text{H}_5$. It is a mobile oil of faint and not unpleasant odor, b.p. 128.5°C . at 15–16 mm. It does not markedly oxidize in air at room temperature, and remains unchanged for months in the light. The following values have been reported for its density and refractive index: d_4^{20} , 1.2997; d_4^{30} , 1.2896; d_4^{20} , 1.2794; d_4^{30} , 1.2694; d_4^{17} , 1.2824; n_D^{17} , 1.6768; $n_F - n_C$ at 17°C ., 0.02434 (123).

Reaction of the magnesium compound of 1,5-dibromopentane (or 1,5-dichloropentane) with phenyldichloroarsine (123) gives a liquid with a faint unpleasant odor, b.p. $153\text{--}154^\circ\text{C}$. at 16–20 mm. It does not markedly oxidize in the air at room temperature. Its density ($20^\circ/4^\circ$) is 1.248; $n_D^{21.4}$, 1.5944; $n_F - n_C$ at 22.4°C ., 0.02167 (124).

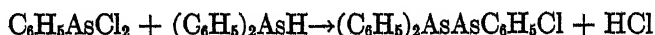
(12) *Action with arsines.* Phenyldichloroarsine reacted with dimethylarsine in a sealed tube filled with carbon dioxide; no pressure was developed. The ether extract of the reaction product gave compact white crystals of dimethylarsinephenylarsine dichloride, $\text{C}_6\text{H}_5\text{AsCl}_2(\text{CH}_3)_2\text{AsH}$, which decompose rapidly when exposed to air, apparently yielding $\text{C}_6\text{H}_5\text{AsClAs}(\text{CH}_3)_2$, an oil (66).

Phenyldimethylarsine combines readily with phenyldichloroarsine to give a colorless addition product, $\text{C}_6\text{H}_5(\text{CH}_3)_2\text{As} \cdot \text{C}_6\text{H}_5\text{AsCl}_2$, which crystallizes from alcohol in colorless needles melting at 36°C . (43).

Blicke and Powers (33) and Steinkopf and Dudek (304) obtained arsenobenzene, $\text{C}_6\text{H}_5\text{As}=\text{AsC}_6\text{H}_5$, m.p. $209\text{--}211^\circ\text{C}$., diphenylchloroarsine, $(\text{C}_6\text{H}_5)_2\text{AsCl}$, m.p. $40\text{--}42^\circ\text{C}$., and tetraphenyldiarsyl, $(\text{C}_6\text{H}_5)_2\text{AsAs}(\text{C}_6\text{H}_5)_2$, m.p. $125\text{--}129^\circ\text{C}$., when phenyldichloroarsine was treated with diphenylarsine, as shown in the following equations:

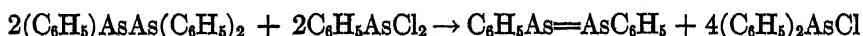


Steinkopf and Smie (310), by condensing phenyldichloroarsine with diphenylarsine, obtained triphenylchlorodiarsine, $(C_6H_5)_2AsAsC_6H_5Cl$, white needles, m.p. $164^\circ C.$:



When phenyldichloroarsine was mixed with an equal weight of bis(α -hydroxyethyl)phenylarsine a slight warming and turbidity was observed, and after one week the mixture was practically solid. The product, after washing, proved to be arsenobenzene, $C_6H_5As=AsC_6H_5$, m.p. $196-199^\circ C.$ (230).

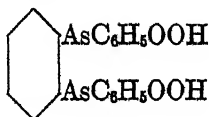
The products resulting from the reaction between tetraphenyldiarsyl and phenyldichloroarsine are arsenobenzene and diphenylchloroarsine (33):



(13) *Action with acids.* Phenyldichloroarsine reacts with chlorosulfonic acid forming benzenesulfonyl chloride, $C_6H_5SO_2Cl$, an oil which crystallizes with difficulty; the crystals melt at $14.5^\circ C.$ (320).

When a neutral solution of diazotized anthranilic acid is condensed with an alkaline solution of phenyldichloroarsine and reduced with sulfur dioxide at $80^\circ C.$ there is formed *o*-carboxydiphenylchloroarsine, a white, crystalline compound melting at $163^\circ C.$ It is readily soluble in alcohol, and moderately soluble in hot benzene (3).

When *o*-aminodiphenylarsonic acid is diazotized and treated with phenyldichloroarsine in 5 *N* sodium hydroxide solution, the product is phenylene-1,2-diphenylarsonic acid

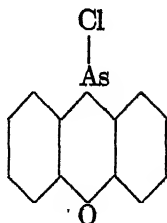


It forms pale yellow microscopic crystals, which do not melt below $310^\circ C.$ It is insoluble in water and the usual organic solvents (197).

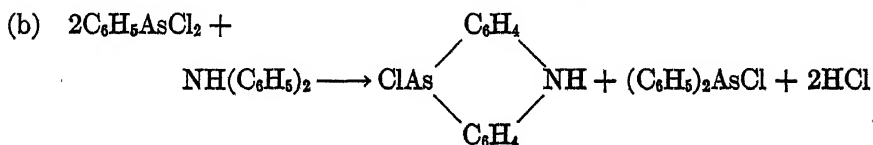
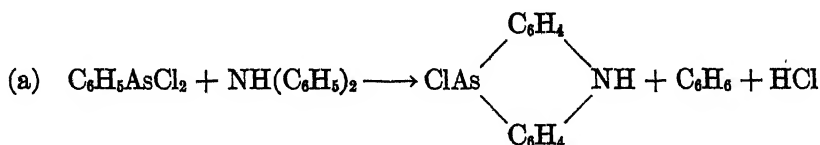
(14) *Action with acid chlorides.* Acetophenone results from the reaction between phenyldichloroarsine and acetyl chloride (191).

Gibson, Johnson, and Vining (114) and Malinovskii (191) found that phenyldichloroarsine was dearsenicated when treated with aluminum chloride and chloroacetyl chloride in carbon disulfide, the product being ω -chloroacetophenone, m.p. $52-55^\circ C.$, b.p. $130-132^\circ$ at 22 mm.

(15) *Action with miscellaneous substances.* Upon condensation of diphenyl ether with phenyldichloroarsine in the presence of aluminum chloride (2) there is obtained 10-chlorophenoxarsine.



Burton and Gibson (51) prepared 10-chloro-5,10-dihydrophenarsazine by heating phenyldichloroarsine with diphenylarsine in the presence of *o*-dichlorobenzene:



The product forms yellow needles melting at 189–190°C.

Upon boiling phenyldichloroarsine for 16 hr. with (a) phenyl-*p*-tolylamine, (b) di-*p*-tolylamine, (c) phenyl- α -naphthylamine there is formed (a) 10-chloro-2-methyl-5,10-dihydrophenarsazine, m.p. 199–200°C. (decomposition), (b) 10-chloro-2,8-dihydrophenarsazine, m.p. 261–262°C., and (c) *N*-chloro-7,12-dihydrobenzophenarsazine, m.p. 218–219°C.

Chloroacetanilide when added to a solution of phenyldichloroarsine in 10 *N* sodium hydroxide produces phenylarsinoacetanilide, $C_6H_5As(O_2H)-CH_2CONHC_6H_5$, which crystallizes from water in small needles, m.p. 182–183°C. (decomposition) (266).

Phenyldichloroarsine in 10 *N* sodium hydroxide solution reacting with chloroacetophenetidine forms phenylarsinoacetophenetidine, $C_6H_5As(O_2H)-CH_2CONHC_6H_4OC_2H_5$ (*p*), which crystallizes from alcohol in needles, m.p. 175°C. (decomposition) (266).

Reaction between β -phenoxyethyl bromide and phenyldichloroarsine in 10 *N* sodium hydroxide solution forms β -phenoxyethylphenylarsinic acid, $C_6H_5As(O_2H)CH_2CH_2OC_6H_5$, which separates first as an oil but soon crystallizes; it melts at 122–123°C. (266).

Addition of an alcoholic solution of chloropicrin dropwise to an alcoholic solution of the sodium salt of phenyldichloroarsine gives phenylarsinic acid, m.p. 158–159°C. (369).

Physiological action

LaCoste and Michael (180) found phenyldichloroarsine violently corrosive to the skin. In contact with the skin of dogs it produces hyperemia, swelling, edema, ulceration, necrosis, etc.; it produces similar changes, together with vesication, on human skin (134). Flury (96) found that intense cell poisoning is caused by phenyldichloroarsine when cells are in contact with it either in stable fluid form or as a gas. Plant cells are similarly affected. It differs from strong caustics in that it produces marked inflammatory reactions and necrosis in the lowest concentrations. The irritant action upon sensory nerves is quite pronounced. The irritating effect is not due to the splitting off of acids or to the action of hydrogen ions. Gilchrist and Matz (116) found that the physiological action of the arsenicals consists in congestion of the mucous membrane of the nose, throat, and bronchi, and edema of the lungs. Occasionally motor and sensory nerve changes are observed, from which recovery is rapid and uniform. Fegler (94) observed that when phenyldichloroarsine in the form of lecithin emulsions was intravenously injected into dogs in doses of 3 mg. per kilogram of weight a violent apnea and a sudden drop in blood pressure occurred; after vagotomy, however, it had no effect on blood pressure or respiration.

Test

According to Blicke and Oakdale (33) the following experiment illustrates the serviceability of the piperidine salt of dithiocarbamic acid as a reagent for the identification of a small quantity of phenyldichloroarsine. To one drop (0.0306 g.) of the latter compound there was added 0.127 g. (five times the calculated amount) of the piperidine salt dissolved in about 3 cc. of dry benzene. The mixture was protected from moisture, and after 12 hr. the benzene was allowed to evaporate. The crystalline residue was washed with water until the piperidine chloride and excess piperidine salt of dithiocarbamic acid had been completely removed. The crude product weighed 0.022 g. After recrystallization from ethyl acetate the product melted at 173–174°C.

Nametkin and Nekrasov (230) found that when 1 cc. of a 0.1 per cent aqueous solution of phenyldichloroarsine was treated with two to three drops of saturated hydrogen sulfide water a distinct turbidity was formed (due to C_6H_5AsS). The test was less satisfactory in alcoholic solutions. Solutions of mercurous nitrate in phenyldichloroarsine did not oxidize the arsenic compound even after long standing, but if the solution was heated, oxidation was brought about and free mercury was formed.

Flury (95) devised a method for the determination of phenyldichloro-

arsine in a mixture of other phenyl derivatives of arsenious acid. This method is dependent upon the degree of oxidation by iodine.

Uses

Schmidt, Steindorff, Fluss, and Schaffrath (301) used phenyldichloroarsine for treating seed grain for parasites.

U. S. patent 1,686,582 (October 9, 1928) was issued to Stoltzenberg (329) for the use of phenyldichloroarsine in destruction of *Opuntia* by action as vapor or spray or by injection of a 5 per cent solution in cresol or sulfuric acid. Steindorff and Schwabe (317) obtained German patent 493,147 (June 26, 1930) for the treatment of grain with phenyldichloroarsine and other arsenic compounds. Walker (350) obtained U. S. patent 1,758,958 (May 20, 1930) for a compound suitable for combating marine borers; it comprises a petroleum oil containing an arsenical compound (phenyldichloroarsine) which is toxic to marine borers and has a solubility of 0.7 to 60 parts in 100,000 parts of sea water at 20°C.

II. CHLOROSULFONIC ACID, ClSO_2OH

In 1854 A. W. Williamson (360) defined, if he did not discover, chlorosulfonic acid, ClSO_2H or ClSO_2OH . It attracted some attention at that time because of the old theory of types, as it was the first example of a mixed type—the water type and the hydrochloric acid type—with the bivalent SO_2 radical. The name “chlorohydrines” was applied to combinations of this mixed type, so that chlorosulfonic acid is also called sulfuric chlorohydrin; it has also been called chlorohydrated sulfuric acid and chlorohydrosulfurous acid.

Preparation

Williamson prepared chlorosulfonic acid by the direct action of hydrochloric acid on sulfur trioxide (362) and by passing a vigorous stream of hydrogen chloride into fuming sulfuric acid (370). Beckurtz and Otto (13), Claesson (55, 56), Michaelis and Schifferdecker (217), Müller (227), Briggs (44), Behrend (16, 17), Pytasz and Rabek (265), Bert (23), and Sanger and Riegel (293, 294) obtained chlorosulfonic acid in a similar manner. Müller (227) also prepared the acid by distilling fuming sulfuric acid with phosphorus pentoxide in a current of hydrogen chloride. Williamson (362, 363), Williams (358, 360), Dewar and Cranston (79, 80), Baumstark (9), and Michaelis (206, 207) obtained chlorosulfonic acid by the action of phosphorus trichloride, phosphorus pentachloride, or phosphoryl chloride on concentrated sulfuric acid; Thorpe (335) heated a mixture of phosphoryl chloride and concentrated sulfuric acid. Williamson (362, 363) obtained chlorosulfonic acid by the action of chlorine on

sulfur chloride or concentrated sulfuric acid; Moureu (226) by the action of sulfuric acid on thionyl chloride; Odling (235), Thomsen (332), and Carrara (52) by the action of moisture on sulfuryl chloride; Michaelis (208) by the action of a little water or concentrated sulfuric acid on sulfuryl chloride; Billitz and Heumann (29) and Ogier (239) by the action of water on pyrosulfuryl chloride; Railton (267) and Odling (257) by the action of imperfectly dried chlorine on moist sulfur dioxide in the presence of platinum black at red heat. Ogier (239) prepared chlorosulfonic acid by the action of gaseous hydrogen chloride on solid sulfur dioxide. Michaelis (208) prepared it from fuming sulfuric acid by the action of phosphorus oxychloride; Geuther (112) by the action of phosphorus trichloride; Thomsen (332) and Carrara (52) by the action of sulfuryl chloride; Sanger and Riegel (293) by the action of pyrosulfuryl chloride; Billitz and Heumann (29) by the action of sulfur oxytetrachloride. Beckurtz and Otto (13), Behrend (16), Müller (227), and Williams (358) obtained chlorosulfonic acid by the action of concentrated sulfuric acid on sulfur monochloride. Lepin (184) and Erdmann (90) obtained the acid by the action of carbon tetrachloride on fuming sulfuric acid. Even chlorine alone will act on sulfuric acid giving chlorosulfonic acid (13, 16, 227, 358). Melsens (202) produced chlorosulfonic acid by passing sulfur dioxide and chlorine into glacial acetic acid or by using charcoal as a catalyst.

The Société pour l'Industrie Chimique à Bale (313) obtained British patent 393,546 (June 8, 1933) for the preparation of chlorosulfonic acid by causing sulfur and chlorine, or a sulfur chloride, if necessary, in the presence of chlorine, to act upon a mixture of sulfuric acid and sulfur trioxide. Krummenacher (178) obtained U. S. patent 1,898,879 (February 21, 1932), French patent 740,944 (August 8, 1932), a British patent (December 8, 1932), and German patent 574,001 (April 7, 1933) for the preparation of the acid by causing one equivalent proportion of a metal chloride, such as sodium chloride, to react with a solution of approximately 2 moles of sulfur trioxide in approximately 1 mole of sulfuric acid. Dachlauer (67) obtained German patent 543,758 (May 25, 1929) for the preparation of the acid by uniting sulfur trioxide with hydrogen chloride at a temperature between 70° and 100°C. McKee and Salls (200) obtained U. S. patent 1,554,870 (September 22, 1924) for the preparation of chlorosulfonic acid by heating sulfuryl chloride and sulfuric acid in the presence of a mercury compound or of salts of antimony, tin, or bismuth. Briggs (44) obtained U. S. patent 1,422,335 (July 11, 1921) for a process of manufacture of chlorosulfonic acid, using contact sulfuric gas and dry hydrogen chloride. Schedler and Marchant (298) obtained British

patent 131,024 (March 25, 1918) for the preparation of the acid by passing hydrogen chloride obtained as a by-product in the chlorination of organic compounds such as benzene, toluene, etc. into sulfuric acid containing about 80 per cent sulfur trioxide. The Sankyô Joint Stock Company (296) obtained Japanese patent 31,580 (October 4, 1917) for the preparation of chlorosulfonic acid by passing chlorine into concentrated sulfuric acid in the presence of sulfur or sulfur monochloride or of substances which yield them by the action of chlorine. Klages and Vollberg (168) obtained U. S. patent 613,181 (January 2, 1912) for the making of chlorosulfonic acid. Saccharin-Fabrik Aktiengesellschaft vorm Fahlberg, List & Co. (290) obtained German patent 228,424 (September 5, 1907) and British patent 16,518 (July 11, 1910) (291) for the manufacture of chlorosulfonic acid by allowing hydrogen chloride gas to act on a solution of sulfur trioxide or by simultaneously leading hydrogen chloride gas and gaseous sulfur trioxide into chlorosulfonic acid.

Physical properties

Chlorosulfonic acid is a colorless, fuming liquid of sharp, unpleasant odor. Its boiling point has been reported as follows: 60–64°C. at 2.4 mm. (294); 74–75°C. at 19 mm. (293); 78°C. at 21–22 mm. (348); 145°C. at 760 mm. (362); 150–151°C. at 775 mm. (348); 150.7–152.7°C. at 760 mm. (13); 151–152°C. at 765 mm. (293, 294); 153.3–153.6°C. at 760 mm. (335); 156°C. at 760 mm. (265); 158.4°C. at 760 mm. (208). Clausnizer (58) found that the boiling point is reduced by 1°C. when the pressure is reduced by 20.6 mm. Chlorosulfonic acid melts at –81° to –80°C. (293, 294).

The specific gravity of chlorosulfonic acid has been reported as follows: 1.784 at 4°C. (293, 294); 1.7874 at 4°C. (335); 1.7875 at 25°C. (348); 1.776 at 18°C. (208); 1.753 (293, 294); and 1.5487 at 155.3°C. (335). Baumstark (9) determined the vapor density as 4.08–4.12, the calculated value being 4.04 at 216°C.; Heumann and Kochlin (140) found the vapor density to be 2.39–2.42 at 184.4°C., 2.09 at 444°C., and 2.40 at 180–216°C. (141); Ogier (239) determined the vapor density as 2.36–2.46 between 180°C. and 216°C. Ogier gave 0.282 for the specific heat of chlorosulfonic acid between 15°C. and 80°C., 12.8 cal. for its heat of vaporization, and 40.3 cal. for its heat of solution in water. Meyer (205) and Matossi and Aderhold (195), using the k-line ($\lambda = 5460 \text{ \AA.}$) of the mercury spectrum in determining the Raman frequencies of sulfur in chlorosulfonic acid found them to be as follows: 194, 300, 410, 498, 606, 920, 1183, 1430. Walden found that chlorosulfonic acid has low ionizing power: $\lambda = 0.160 \times 10^{-18}$ at 25°C.

Thorpe (335) made observations of the rate of expansion of chloro-

sulfonic acid in a dilatometer when heated in a water bath (see table 3). The values gave the formula:

$$V = 1 + 0.00090505t + 0.00000018747t^2 + 0.000000002394t^3$$

Assuming that this formula may be taken to represent the expansion of chlorosulfonic acid from 0°C. to its boiling point, table 4 gives the relative volume at every 5° between 0° and 160°C.

Lutschinsky (190) using Batschinsky's formula, $\eta = c/v - \omega$, where η is the viscosity, v is the specific volume, and ω is a constant for the given

TABLE 3
Rate of expansion of chlorosulfonic acid

| Δ | OBSERVED | CALCULATED | Δ | OBSERVED | CALCULATED |
|----------|----------|------------|----------|----------|------------|
| 10.93 | 3377.2 | 3377.7 | 64.42 | 3538.3 | 3538.5 |
| 25.34 | 3420.8 | 3420.5 | 73.90 | 3567.5 | 3567.9 |
| 36.64 | 3454.4 | 3454.2 | 89.05 | 3615.6 | 3615.7 |
| 48.51 | 3489.6 | 3489.9 | 100.05 | 3650.7 | 3651.1 |

TABLE 4
Relative volumes of chlorosulfonic acid

| t | VOLUME | t | VOLUME | t | VOLUME | t | VOLUME |
|-----|---------|-----|---------|-----|---------|-------|---------|
| °C. | | °C. | | °C. | | °C. | |
| 0 | 1.00000 | 40 | 1.03655 | 85 | 1.07926 | 130 | 1.12492 |
| 5 | 1.00453 | 45 | 1.04118 | 90 | 1.08416 | 135 | 1.13024 |
| 10 | 1.00906 | 50 | 1.04585 | 95 | 1.08910 | 140 | 1.13560 |
| 15 | 1.01361 | 55 | 1.05053 | 100 | 1.09409 | 145 | 1.14103 |
| 20 | 1.01817 | 60 | 1.05525 | 105 | 1.09911 | 150 | 1.14651 |
| 25 | 1.02274 | 65 | 1.05999 | 110 | 1.10418 | 155 | 1.15205 |
| 30 | 1.02732 | 70 | 1.06476 | 115 | 1.10929 | 160 | 1.15765 |
| 35 | 1.03193 | 75 | 1.06956 | 120 | 1.11445 | 155.3 | 1.15238 |
| | | 80 | 1.07439 | 125 | 1.11966 | | |

liquid, has confirmed it for chlorosulfonic acid, c being 0.000698 and ω being 0.5440 (see table 5).

Equilibria involving chlorosulfonic acid

At 170°C. the reaction,



is a reversible one, and after 72 hr. the equilibrium mixture contains 1 mole of SO_2Cl_2 , 1 mole of H_2SO_4 , and 2.5 moles of ClSO_3H . Sulfur dioxide and chlorine are not formed between 170° and 190°C., although at a higher

temperature they begin to be noticeable. Obviously, therefore, the sulfonyl chloride is not formed by the union of sulfur dioxide and chlorine initially produced by complete dissociation of the chlorosulfonic acid, but is a direct decomposition product; this is emphasized by the fact that when the formation of the sulfonyl chloride occurs at the boiling point of the chlorosulfonic acid, owing to the presence of a catalytic agent, its amount is not increased by the passage of a current of chlorine and sulfur dioxide through the liquid. The production of sulfur dioxide and chlorine at a high temperature is due to decomposition in the sense of the equation (284):



With methyl sulfate, the simplest equation is

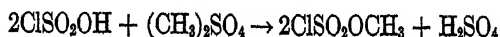
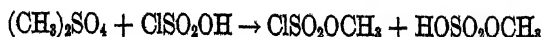


TABLE 5
Viscosity of chlorosulfonic acid

| <i>t</i> | η | <i>t</i> | η | <i>t</i> | η | <i>t</i> | η |
|----------|--------|----------|--------|----------|--------|----------|--------|
| °C. | | °C. | | °C. | | °C. | |
| -10 | 0.0563 | 10 | 0.0329 | 26 | 0.0239 | 42 | 0.0185 |
| -5 | 0.0493 | 12 | 0.0316 | 28 | 0.0230 | 44 | 0.0179 |
| -2 | 0.0454 | 14 | 0.0302 | 30 | 0.0223 | 46 | 0.0174 |
| 0 | 0.0424 | 16 | 0.0289 | 32 | 0.0215 | 48 | 0.0169 |
| 2 | 0.0401 | 18 | 0.0276 | 34 | 0.0209 | 50 | 0.0166 |
| 4 | 0.0383 | 20 | 0.0266 | 36 | 0.0203 | 55 | 0.0158 |
| 6 | 0.0364 | 22 | 0.0257 | 38 | 0.0196 | 60 | 0.0151 |
| 8 | 0.0347 | 24 | 0.0248 | 40 | 0.0189 | | |

but the reaction is actually more complicated and does not go quantitatively as indicated in the equation (186). In sealed tubes at room temperature an equimolar mixture reacts according to the equation



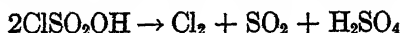
Equilibrium is reached in about one month, and the mixture then contains 1 mole of each product to 2 moles of each of the initial substances. The ratio of $\text{ClSO}_2\text{OCH}_3$ formed to that which would be formed if the reaction were not reversible (r) = 0.36. If one of the initial substances is employed in 80 per cent excess, r = 0.07 after 27 hr., and 0.25 after 108 hr.; at 30°C. after 62 hr., r = 0.09; at 40°C. after 80 hr., r = 0.36. After a certain period acidity increases as a result of the reaction



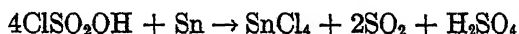
At room temperature this reaction is incomplete after 138 hr., but its velocity increases rapidly with temperature; after 20 hr. the same final state is reached whether at 70°C. or at 100°C. The ratio $r = 0.54$, and about 5 per cent of sulfuric acid is formed. Upon distillation under reduced pressure of the mixture of sulfate and chlorosulfonic acid about 50 per cent of the methyl chlorosulfonate is recovered, the chlorosulfonic acid is practically all lost, and sulfuric acid accumulates up to 20 per cent (41).

Chemical properties

(1) *Heating.* Upon heating chlorosulfonic acid in a sealed tube to 170–180°C., decomposition takes place as follows (13):



(2) *Action with elements.* Chlorosulfonic acid does not react with sulfur in the cold, but on warming a brisk reaction takes place, with the production of sulfur dioxide, hydrogen chloride, and sulfur dichloride. With phosphorus a violent reaction takes place, not infrequently accompanied by an explosion when the chlorosulfonic acid is warmed; sulfur dioxide and hydrogen chloride are given off. With amorphous phosphorus the action is quieter; the products are phosphorus oxychloride and phosphoric acid. Chlorosulfonic acid reacts with finely powdered arsenic with evolution of sulfur dioxide; arsenic trichloride distills off and arsenious oxide remains behind. Antimony behaves in a similar manner. Tin acts in the cold with production of tin tetrachloride in theoretical quantity according to the equation:



When chlorosulfonic acid is heated with charcoal it is decomposed, with evolution of sulfur dioxide, hydrogen chloride, and carbon dioxide. Chlorosulfonic acid acts as a chlorinating agent with sulfur, arsenic, antimony, and tin (140).

(3) *Action with salts.* Thorpe (336) found that chlorosulfonic acid acts with great violence on silver nitrate, forming silver chloride and nitroxy-chlorosulfonate, $\text{NO}-\text{O}-\text{SO}_2-\text{Cl}$.

By the action of chlorosulfonic acid on potassium chromate Heumann and Koechlin (141) obtained chromyl chloride.

Chlorine is evolved when a small quantity of fused potassium nitrate is treated with chlorosulfonic acid. Subsequently, on applying heat, nitrogen peroxide is given off in large quantity. No other substances save these two could be detected, even when considerable quantities of the materials were employed in equivalent proportions, and the evolved vapors

were passed through a condenser cooled to -18°C . At first chlorine alone escaped and no liquid condensed, but on the application of heat red vapors were formed, which, on passing into the condenser, gave a small quantity of a deep red liquid,—a solution of chlorine in nitrogen peroxide. The issuing gas on being passed into hot water gave chlorine; with cold water hydrogen chloride was produced, owing to the oxidation of the chlorine of the nitrous acid formed by the solution of the peroxide in water (359).

Upon treating sodium acetate with chlorosulfonic acid in a little acetic anhydride there is formed acetic anhydride (265).

Ruff (284) found that sodium chloride dissolves in chlorosulfonic acid with evolution of hydrogen chloride and production of the sodium salt, ClSO_3Na , which is precipitated by the addition of sulfuryl chloride and is readily decomposed by water.

Mercuric salts rapidly decompose chlorosulfonic acid at its boiling point into sulfuryl chloride and sulfuric acid; several other salts effect a similar result, only more slowly. The figures after the names of the following salts indicate the number of grams of sulfuryl chloride formed by boiling 50 g. of the acid for 1 hr. with 1 g. of the salt. Mercuric chloride, 13.0; mercuric sulfate, 13.0; antimony pentachloride, 7.5; antimony trichloride, 7.5; stannic chloride, 5.8; bismuth chloride, 3.3; platonic chloride, 2.5; uranyl chloride, 1.7; gold chloride, 1.2; copper sulfate, 0.8; tungsten chloride, 0.8; lead chloride, 0.7; cobalt sulfate, 0.5; magnesium chloride, 0.5. The chlorides of zinc, aluminum, iron, calcium, and sodium are without action. As the whole of the chlorosulfonic acid is easily decomposed by boiling with mercuric chloride, the method is probably capable of commercial application for the manufacture of sulfuryl chloride. The mercuric chloride is not changed at all in the action, but the sulfate is converted into mercuric chloride (284).

(4) *Action with oxides and chlorides.* When chlorosulfonic acid was treated with a dehydrating agent such as phosphorus pentoxide, Ogier (239) obtained pyrosulfuryl chloride, $(\text{ClSO}_2)_2\text{O}_2$.

By heating chlorosulfonic acid with phosphorus pentachloride pyrosulfuryl chloride is formed (208).

On cooling a warm solution of titanium, antimony, or selenium tetrachlorides in chlorosulfonic acid there is formed the corresponding sulfo-tetrachloride. Sulfoantimony oxytetrachloride, $\text{ClSO}_2\text{OSbCl}_4$, boils at $150\text{--}151^{\circ}\text{C}$. at 726 mm.; the boiling point falls 1°C . with a decrease in pressure of 20.6 mm (60). Sulfotitanium oxytetrachloride, $\text{ClSO}_2\text{OTiCl}_4$, when dried at 100°C ., is an amorphous powder. It is soluble in water with evolution of chlorine and sulfur dioxide. It fumes on exposure to damp air, and is converted into a moist white mass which is no longer

soluble in water (60). Sulfoselenium oxytetrachloride, $\text{ClSO}_2\text{OSeCl}_3$, is deposited in groups of needle-shaped crystals which melt at 165°C . and boil at 183°C .; it is very deliquescent (56, 60).

Selenium oxide reacting with chlorosulfonic acid forms selenium oxychloride and pyrosulfuric acid (58). The oxychloride reacting with chlorosulfonic acid forms selenium tetrachloride and pyrosulfuric acid (58).

(5) *Action with hydrocarbons.* Ethylene is readily absorbed by chlorosulfonic acid yielding a colorless liquid, ethyl chlorosulfonate, boiling at $93\text{--}95^\circ\text{C}$. at 100 mm. Its vapor possesses a pungent odor and produces a copious flow of tears. Ethyl chlorosulfonate is heavier than water. It fumes when exposed to the air. It is decomposed by water slowly in the cold and rapidly when heated, with formation of hydrogen chloride, sulfuric acid, and ethyl alcohol. Hot aqueous potassium hydroxide and cold alcoholic potassium hydroxide solutions readily decompose it, ethyl chloride being evolved. It dissociates without decomposition in pure ether, but with ethyl (or amyl) alcohol it evolves ethyl chloride and ethylsulfuric acid (or amylsulfuric acid) (227).

Chlorosulfonic acid is used as a catalyst in the polymerization of cyclopentadiene. The reaction takes place violently with the formation of phenylsulfonic acid (316).

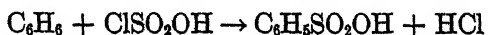
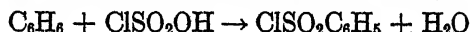
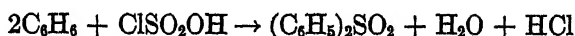
When *n*-hexane and isohexane were treated with equal volumes of chlorosulfonic acid, the isohexane became warm and in a few minutes bubbles of hydrogen chloride were rapidly evolved; the normal hexane did not rise perceptibly in temperature, and it was only after some time that hydrogen chloride was given off. Heptane and octane were similarly treated, and similar results were obtained.

The results obtained are sufficient to show that chlorosulfonic acid in the cold, like fuming nitric acid at higher temperatures, acts far less energetically on the normal paraffins than on the isoparaffins, and also less energetically on the polymethylenes than on their methyl derivatives. Generally chlorosulfonic acid acts more energetically on hydrocarbons that contain a $\equiv\text{CH}$ group than on others (363).

Benzene, treated with 10 parts of chlorosulfonic acid at $150\text{--}160^\circ\text{C}$. for 2 hr., gives *m*-benzenedisulfonyl chloride, $m\text{-C}_6\text{H}_4(\text{SO}_2\text{Cl})_2$, and diphenylsulfonedisulfonyl chloride, melting at $174\text{--}175^\circ\text{C}$., together with a small amount of *p*-benzenedisulfonyl chloride, $p\text{-C}_6\text{H}_4(\text{SO}_2\text{Cl})_2$. When 4 parts of benzene and 3 parts of the acid are heated to boiling for 10 min., then 40 parts of the acid are added and the mixture heated to $150\text{--}160^\circ\text{C}$. for 5 hr., diphenylsulfonedisulfonyl chloride is formed. Benzene, when heated with 40 parts of chlorosulfonic acid for 7 hr. at $140\text{--}150^\circ\text{C}$., gives diphenylsulfonyl chloride (257).

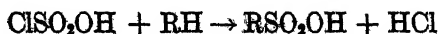
Armstrong (5) found that when chlorosulfonic acid reacts with benzene

the chief products are sulfobenzide, sulfobenzoic chloride, and sulfobenzolic acid, as shown in the following equations:

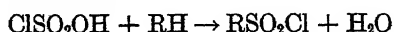


Toluene and 8 parts of chlorosulfonic acid, when heated for 5 hr. at 140–150°C., give 2,4-(ClO₂S)₂C₆H₃CH₃, m.p. 52°C. Toluene, treated with a molecular amount of chlorosulfonic acid and heated for a short time, then treated with a large excess of chlorosulfonic acid and heated for 5 to 6 hr. at 150–160°C., gives di(*p*-methylphenyl-*m*-sulfonyl chloride) sulfone, m.p. 177–178°C. (257). The action of chlorosulfonic acid upon toluene at low temperatures (–35° to –40°C.) gives a very small yield of a mixture containing from 53 to 58 per cent of the *p*-isomer. If the mixture is made at –40°C. and then allowed to warm to 5–10°C., the yield is increased, while the per cent of the *p*-isomer is about 52 per cent. As the temperature rises the per cent of the *p*-isomer increases (–15°C., 57.5 per cent; 5–10°C., 73 per cent; 20–25°C., 76.5 per cent; 35–40°C., 86 per cent; 75–80°C., 94.5 per cent). When these facts are considered in connection with the further fact that with 1 mole of chlorosulfonic acid the main product is the acid, but with an excess of chlorosulfonic acid the main product is the chloride, it appears that the reaction takes place in two steps, and that it is essential in obtaining good yields of the chloride to allow the mixture to stand a sufficient length of time to complete the second reaction. This is important, since incomplete investigations show that the acids are not proportionately converted into the acid chlorides in dilute solutions of chlorosulfonic acid, but that the predominating acid is more quickly transformed. Any local excess of toluene should be avoided if the *o*-isomer is required in maximum yield. This is met by spraying the toluene into the acid. There is an early limit to the effect of temperature on the yield of the *o*-isomer, as is seen in the fact that the yield is lower at –40°C. than at 5–10°C. (141).

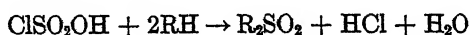
When 1 mole of the acid to 1 mole of the hydrocarbon was used, the products of the reaction were sulfotoluide, *p*-toluenesulfonyl chloride, and *p*-toluenesulfonic acid; the latter occurring in largest quantity. Since sulfotoluide results from the reaction of 1 mole of the acid and 2 moles of toluene, the presence of some undecomposed chlorosulfonic acid, also observed in the product of the reaction, is accounted for. Toluenesulfonic acid being the chief product, the essential reaction would appear to be that indicated as follows:



At the same time the formation of this compound may be explained from the decomposition of toluenesulfonyl chloride by water, indirectly, therefore, according to the equation:



The proof that such is actually the case was afforded by a second experiment, in which the reaction was allowed to proceed in the presence of phosphorus pentoxide; the quantity of the sulfonyl chloride was thereby much increased. It is therefore concluded that in the case of toluene both of the decompositions represented by the two equations given above occur, and to a like extent; the reaction indicated below also occurs, but only to a very limited extent (14):

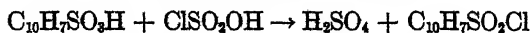


It was found by Holleman and Caland (80) that the action of chlorosulfonic acid on toluene forms *p*-toluenesulfonic acid, $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3\text{H}$.

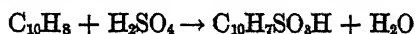
o-Xylene and chlorosulfonic acid heated for 5 hr. at 150–160°C. gave 1,2,3,5-(CH_3)₂ $\text{C}_6\text{H}_2(\text{SO}_2\text{Cl})_2$ melting at 79°C.; *m*-xylene and chlorosulfonic acid gave di-*m*-xylyl sulfone, m.p. 121°C.; *p*-xylene also gave a sulfone, di-*p*-xylyl sulfone, m.p. 142°C. (257).

When naphthylene was heated with chlorosulfonic acid at 180°C. for 10 hr., tetrachlorophthalic anhydride, m.p. 255°C., was formed (351).

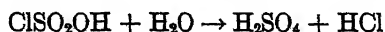
Corbellini (63) found chlorosulfonic acid to behave with naphthalene as a chlorosulfonating agent. When solid naphthalene was treated at 15–45°C. with chlorosulfonic acid (2 moles), 1,5- $\text{C}_{10}\text{H}_6(\text{SO}_3\text{H})_2$ was formed, together with varying proportions of the corresponding disulfonyl chloride. When carbon tetrachloride was used as a diluent and the hydrocarbon (1 mole) was treated with either 2 or 4 moles of the acid, sulfonyl chlorides were always formed in addition to the mono- and the di-sulfonic acids. In all cases the hydrocarbon was attacked only in the 1- and 5-positions. It is probable that the first phase of the reaction consists in the formation of the sulfonic acid, which then passes to the chloride,



these changes being accompanied by the secondary reactions,



and



The final yields of the various products evidently depend on the velocities of these different reactions, these being governed by the conditions employed. The sulfochlorinating action is favored by low temperatures.

When the reaction was prolonged it continued with the formation of

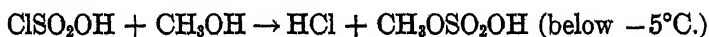
other products. Naphthalene was added slowly to chlorosulfonic acid at 5–10°C. (abundant evolution of hydrogen chloride), the mixture allowed to stand for 120–140 hr. at 50–55°C. (sulfur dioxide evolved), and then poured on ice; the precipitate was washed with water by decantation, and then filtered, and the residue was recrystallized from benzene. The product was 1,5-naphthalenedisulfonyl chloride, $1,5\text{-C}_{10}\text{H}_6(\text{SO}_2\text{Cl})_2$, m.p. 183°C. With a greater excess of chlorosulfonic acid at elevated temperature the reaction proceeded more rapidly and the yield was higher (65). Naphthalene and 10 parts of chlorosulfonic acid, acting a short time at 0°C., gave the disulfonyl chloride, m.p. 183°C. (257).

Diphenyl and 5 parts of chlorosulfonic acid, heated at 50°C. for 12 hr., gave diphenylmonosulfonic acid, m.p. 138°C.; the hydrocarbon and acid in the same ratio at 18°C. for 24 hr. gave *o,o'*-biphenylenesulfone-*p,p'*-disulfonyl chloride, m.p. 236°C. (257).

When a slight excess of an aqueous solution of chlorosulfonic acid was slowly added to a cooled chloroform solution of diphenylmethane, a monosulfonic acid was formed; from the chloroform solution diphenylmethane-*o*-sulfone was obtained (299).

(6) *Action with alcohols.* If methyl alcohol be allowed to drop slowly into chlorosulfonic acid surrounded by ice, an energetic action takes place. If the acid is added to the alcohol, the same reaction takes place but a portion of the hydrogen chloride reacts with the alcohol, producing the chloride and water. If the temperature be allowed to rise during the action, a considerable amount of ethyl chlorosulfonate is produced, $\text{ClSO}_2\text{OC}_2\text{H}_5$. This is an oily liquid which does not solidify at -30°C .; it is soluble in absolute ether (55).

Levillant and Simon (185) found that in the Claesson-Ullman process the following reactions take place:



If, however, chlorosulfonic acid and methyl chlorosulfonate are heated to 90–100°C. for several hours and the product is fractionated *in vacuo*, methyl chlorosulfonate begins to boil at 40°C. at 16 mm., most of it passing over at 50–55°C. together with a little chlorosulfonic acid; if the bath is next heated to 190–200°C., unchanged chlorosulfonic acid passes over, accompanied by a little methyl chlorosulfonate and some methyl sulfate, while the residue is mainly sulfuric acid. When various proportions were used, the yield of methyl chlorosulfonate varied from 0.4 to 0.6 mole. The reaction



is also believed to take place. The crude methyl chlorosulfonate is a colorless liquid, boiling at 42°C. at 16 mm. and at 134–135°C. at 760 mm. with some decomposition. Its density is 1.514 at 0°C. and 1.492 at 15°C.; n_D^{17} , 1.414. It solidifies in a mixture of carbon dioxide and acetone, and melts at about -70°C. It is strongly lachrymatory. It does not mix with sulfuric acid, but is miscible with its chlorine and methyl derivatives, as well as with many organic solvents (185).

In the action of chlorosulfonic acid upon ethyl alcohol, ethyl sulfate is formed. It is a faint yellow inodorous liquid which dissolves in water in all proportions with formation of ethylsulfuric acid, but in alcohol without undergoing any change; it is miscible with ether and benzene, but is reprecipitated by excess (241). McIntosh (199) found that at low temperatures, -50° to -80°C., chlorosulfonic acid forms ethyl hydrogen sulfate and hydrogen chloride in reacting with ethyl alcohol.

Walter (351) found that when glycerol is heated with chlorosulfonic acid at 100–170°C. there results a glyptal resin.

(7) *Action with phenols.* Chlorosulfonic acid is added to phenol in carbon disulfide, and the mixture is cooled to -15°C. and stirred; after 2.5 hr. the carbon disulfide is decanted, and by proper treatment there is separated phenylsulfuric acid, $C_6H_5SO_3H$, and *p*-phenolsulfonic acid, $p-HOC_6H_4SO_3H$ (48). Equivalent quantities of phenol and chlorosulfonic acid give phenol-2,4-disulfonyl chloride, m.p. 89°C.; after heating the above substances at 130–140°C. for 4 to 5 hr. the product is phenol-2,4,6-trisulfonyl chloride, m.p. 193°C. (256). Orłowsky (241) prepared phenyl sulfate by the action of phenol on chlorosulfonic acid; it is a thick, oily, more or less dark-colored liquid which decomposes at once in water.

Burkhardt (48) obtained *p*-tolylsulfuric acid, $CH_3C_6H_4SO_3H$, by adding chlorosulfonic acid to a carbon disulfide solution of *p*-cresol. Pollak, Gebauer-Fuelnegg, and Riesz (256) obtained 2-hydroxytoluene-3,5-disulfonyl chloride (*o*-cresol-4,6-disulfonyl chloride), m.p. 85–86°C., when *o*-cresol and chlorosulfonic acid, either in equivalent amounts or with excess acid, were allowed to react at room temperature. *m*-Cresol gives *m*-cresol-4,6-disulfonyl chloride, m.p. 84–89°C. If the equivalent amount of chlorosulfonic acid is added to *m*-cresol there is formed principally *m*-cresolsulfonic acid, but also di-*m*-cresyl sulfate, m.p. 119°C. Heating *o*-cresol with chlorosulfonic acid (10 parts) at 110°C. gives *o*-methylphenylene-*o*-sulfonyl di-*p,p'*-disulfonyl chloride, which decomposes at 280°C., and is stable in boiling water or alcohol. *m*-Cresol and 10 parts of chlorosulfonic acid, heated at 110°C. for 1.25 hr., give *m*-cresolsulfonyl di-sulfonyl chloride, which decomposes at 290°C.; heating for 6 hr. at 130–140°C. and pouring into concentrated hydrochloric acid gives *m*-cresol-2,4,6-trisulfonyl chloride, m.p. 151°C. *p*-Cresol likewise gives *p*-cresol-

sulfonylide disulfonyl chloride, which decomposes at 280°C. Haworth and Lapworth (136), by treating chlorosulfonic acid with a carbon disulfide solution of *m*-cresol at -15°C., formed *m*-tolyl hydrogen sulfate along with *m*-cresol-6-sulfonic acid. *m*-Cresol-4,6-disulfonic acid was produced by the action of 2 moles of chlorosulfonic acid on a carbon disulfide solution of *m*-cresol.

The action of chlorosulfonic acid on catechol for 24 hr. at ordinary temperature yields the disulfonic acid, 1,2,3,5-(HO)₂C₆H₂(SO₃H)₂, but if the reaction mixture is heated at 110°C. for 1.5 hr., catechol-3,5-disulfonyl chloride, m.p. 149-150°C., is obtained. Heated at 150°C. for 8 hr. the reaction mixture yields the neutral sulfate of catechol-3,5-disulfonyl chloride, (SO₂Cl)₂C₆H₂SO₂, m.p. 143°C. (253).

Quinol, treated with 10 parts of chlorosulfonic acid at the ordinary temperature, yields no products which are insoluble in water or hydrochloric acid. Heated with chlorosulfonic acid at 150-160°C. for 8 hr. it yields chloranil, together with by-products which are best obtained by using 50 parts of chlorosulfonic acid and heating for 80 hr.; these products are pentachlorophenol, m.p. 189°C., and *p*-dichlorobenzodiquinoyl (253).

Resorcinol and chlorosulfonic acid in carbon disulfide at 0°C. or at room temperature (using up to five times the theoretical quantity of chlorosulfonic acid) give 1,3-dihydroxybenzene-4,6-disulfonic acid. Ten parts of chlorosulfonic acid with resorcinol at room temperature gives resorcinol-4,6-disulfonyl chloride, m.p. 178-179°C. Resorcinol and 50 parts of chlorosulfonic acid, heated for 2 hr. at 110°C., give resorcinol-2,4,6-trisulfonyl chloride, m.p. 168°C.; resorcinol and 100 parts of chlorosulfonic acid, heated 110 hr. at 160-170°C., give hexachlorobenzene (252).

Chlorosulfonic acid acts on α -naphthol at ordinary temperature, the 2-sulfonic acid derivative crystallizing out. With an excess of chlorosulfonic acid (five times the weight of α -naphthol for 2.5 hr., or ten times the weight for 1.5 hr.) there results 1-naphthol-2,4-disulfonyl chloride, m.p. 149°C. Prolonged action (4 to 5 days) gives 1-naphthol-2,4,7(?)-trisulfonyl chloride, m.p. 172°C. At 100°C. chlorosulfonic acid and α -naphthol give the 4-sulfonic acid derivative; at 160°C., a black product, or with an excess of chlorosulfonic acid, a resinous product, is obtained, from which a trichloronaphthalenesulfonyl chloride, m.p. 214°C., is isolated.

The action of chlorosulfonic acid upon β -naphthol at the ordinary temperature gives only the 1-sulfonic acid derivative; on standing, a mixture of disulfonyl chlorides is obtained. Excess of chlorosulfonic acid yields a mixture of two disulfonyl chlorides, m.p. 111°C. and 177°C. Heating chlorosulfonic acid and β -naphthol at 130-140°C. gives 2-naphthol-3,6,8-trisulfonyl chloride, m.p. 196°C. Heating β -naphthol with 50

parts of chlorosulfonic acid for 80 hr. at 150–160°C. gives a compound containing chlorine but not sulfur, m.p. 120–122°C. (a dichloronaphthalene (?)) and a sulfur-containing compound, m.p. 136–140°C., probably a naphthoquinone derivative (255).

Phloroglucinol, treated with ten times its weight of chlorosulfonic acid at ordinary temperature, yielded the trisulfonic acid, which, however, could not be freed from inorganic acids and was isolated as the ammonium salt. At higher temperatures or with twenty to fifty times the quantity of chlorosulfonic acid, phloroglucinol yielded phloroglucinol-2,6-disulfonyl chloride, m.p. 184°C. The potassium salt of the disulfonic acid, treated with 6 moles of chlorosulfonic acid, was converted into the trisulfonic acid. At 150–160°C. the reaction between phloroglucinol and chlorosulfonic acid yielded pentachlorophenol and hexachlorobenzene (254).

The action of chlorosulfonic acid on pyrogallol for 45 min. at 100°C. yields the disulfonyl chloride, m.p. 178°C. (decomposition); at higher temperatures pentachlorophenol and hexachlorobenzene are obtained (254).

Treatment of *o*-xylenol, 2,3-(CH₃)₂C₆H₃OH, with 10 parts of chlorosulfonic acid at –5°C. to 0°C. for 24 hr. gives 2,3,2',3'-tetramethyldiphenyl-1,6,1',6'-sulfonyl chloride-4,4'-disulfonyl chloride, which decomposes at 295°C., and also 2,3-dimethylphenyl-4,6-disulfonyl chloride, which melts at 104–105°C. *o*-Xylenol with 10 parts of chlorosulfonic acid at –5°C. to 0°C. for 4 hr. gives only water- or hydrochloric acid-soluble products. One part of the alcohol and 10 parts of the acid, heated at 110°C. for 2 hr., give 2,3,2',3'-tetramethyldiphenyl-1,6,1',6'-sulfonyl chloride-4,4'-disulfonyl chloride and 4,4'-disulfonanilide, m.p. 273°C. The 3,4-compound with 10 parts of the acid gives 3,4-dimethylphenol-2,5-sulfonyl chloride, m.p. 72°; the disulfonanilide melts at 160°C.; the free sulfonic acid couples with *p*-O₂NC₆H₄N₂X, giving a bright red solution which dyes animal fibers. The 2,5-compound, 2,5-(CH₃)₂C₆H₃OH, with 10 parts of chlorosulfonic acid gives 2,5-dimethylphenol-3,6-disulfonyl chloride, m.p. 58°C.; the disulfonanilide melts at 173°C.; the free acid gives an orange-yellow dye with *p*-O₂NC₆H₄N₂X. The 3,5-compound, 3,5-(CH₃)₂C₆H₃OH, and chlorosulfonic acid give a mixture in varying proportions, depending upon the temperature of the reaction, of the two disulfonyl chlorides, m.p. 89–91°C. and 117–119°C.; the two disulfonanilides melt at 160–161° and 205–207°C. The 2,4-compound, 2,4-(CH₃)₂C₆H₃OH, gives 2,4-dimethylphenol-6-sulfonyl chloride, m.p. 93–95°C. and 1,3,1',3'-tetramethyldiphenyl-4,5,4',5'-sulfonyl chloride, which decomposes above 300°C. (164).

When a well-cooled chloroform solution of guaiacol is treated with chlorosulfonic acid, there is first formed *o*-methoxyphenyl hydrogen sulfate, but if the mixture be allowed to remain for a few minutes, a white crystalline, deliquescent precipitate of guaiacolsulfonic acid is produced (188).

When thiophenol is allowed to react with chlorosulfonic acid the following reaction takes place (14):



(8) *Action with aldehydes.* Paraformaldehyde (or other formaldehyde-generating compounds) reacts with chlorosulfonic acid below 70°C. to give chloromethyl chlorosulfonate, b.p. 49–50°C. at 14 mm., and methylene sulfonate, m.p. 153°C.; above 70°C. there are obtained chloromethyl sulfate, b.p. 96–97°C. at 14 mm., and dichloromethyl ether, b.p. 101.5–102°C. The chloromethyl chlorosulfonate may be converted by chlorosulfonic acid at 70–80°C. into methylene sulfate. The products are useful as alkylating agents and as insecticides. Fuchs and Katcher (104) obtained German patent 505,687 (October 18, 1928) for this method of preparation.

Distillation of the product resulting from the reaction between chlorosulfonic acid and polymerized formaldehyde gave a mixture of chloromethyl chlorosulfonate and chlorosulfonic acid, boiling at 40–60°C. at 11–14 mm.; when 1.25 mole of chlorosulfonic acid per mole of formaldehyde was used there was obtained, together with the above distillate, a small amount of a higher boiling oil, and the residue in the flask solidified after a time to a cake which proved to be methylene sulfate. With 2.5 moles of chlorosulfonic acid an amount of the formaldehyde corresponding to the methylene sulfate was converted into chloromethyl chlorosulfonate. If, in the reaction between 1.25 moles of chlorosulfonic acid and 1 mole of formaldehyde, the temperature is not allowed to rise above 70–80°C., there is obtained, on pouring upon ice, a heavy oil which, when dried and distilled up to 120°C. under atmospheric pressure, gives hydrogen chloride, polymerized formaldehyde, and a small amount of dichloromethyl ether; distillation of the residue *in vacuo* gives, together with a further small amount of formaldehyde, chiefly dichlorodimethyl sulfate, $(\text{ClCH}_2\text{O})_2\text{SO}_2$; the separation of polymeric formaldehyde is always accompanied by liberation of hydrogen chloride and is to be ascribed to the hypothetical chloromethyl alcohol presumably formed in the reaction. To avoid pouring the reaction product upon ice to destroy the excess chlorosulfonic acid and sulfuric acid, sodium chloride and anhydrous potassium sulfate were used to separate the oil. If the reaction between formaldehyde and chlorosulfonic acid is carried out in the cold and an equivalent amount of sodium chloride is added an almost acid-free oil can be obtained by simple decantation, and distillation gives a materially higher yield of dichlorodimethyl ether. With potassium sulfate instead of sodium chloride, distillation gives, along with dichlorodimethyl ether and dichlorodimethyl sulfate, chiefly chloromethyl chlorosulfonate. Since vacuum distillation of the products of the reaction of chlorosulfonic acid and formaldehyde

gives chloromethyl chlorosulfonate (and methylene sulfate) as the sole water-insoluble substances, it seems likely that dichlorodimethyl sulfate on vacuum distillation with chlorosulfonic acid changes into these compounds; as a matter of fact, from pure dichlorodimethyl sulfate and chlorosulfonic acid was obtained, depending upon the relative amounts of the two substances used, either a mixture of chloromethyl chlorosulfonate and methylene sulfate, or chloromethyl chlorosulfonate alone. Dichlorodimethyl ether reacts with chlorosulfonic acid at 60–70°C. and on distillation yields chloromethyl chlorosulfonate exclusively, but if the product is poured upon ice, there separates a mixture of chloromethyl chlorosulfonate and dichlorodimethyl sulfate (102).

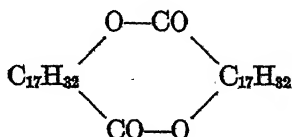
Acetaldehyde and paraldehyde react vigorously with chlorosulfonic acid, yielding dark products which are soluble in water and are not analogous to those derived from formaldehyde. When chloral is treated at room temperature with chlorosulfonic acid, octachlorodiethyl ether, $(\text{CCl}_2\text{CHCl})_2\text{O}$, b.p. 130–131°C. at 11 mm., m.p. 47°C., which separates when the reaction mixture is cooled to -50°C ., is produced; hydrogen chloride and carbonyl chloride are evolved. Metachloral and chloral hydrate give similar results (103).

(9) *Action with acids.* Chlorosulfonic acid reacts with oleic acid to split off hydrogen chloride and form sulfoöleic acid (258).

Upon treating chlorosulfonic acid with undecylenic acid there is formed hydroxysulfoundecanoic acid, free from chlorine. Its analysis by Bauer (8) proves that all sulfo fatty acids, whether produced by chlorosulfonic acid or sulfuric acid, add OH and SO_3H at the double bond of the acid and differ from each other only in the amount added. Pomeranz (259) suggests that a sulfonation of undecylenic acid by means of sulfur trioxide would definitely decide how the sulfonic acid group adds to unsaturated aliphatic acids.

The action of chlorosulfonic acid on $\Delta^{9,10}$ -undecenoic acid in ether gives an oil which loses chlorine when its ether solution is shaken with sodium sulfate, giving 10-hydroxy-11-sulfo- and 11-hydroxy-10-sulfo derivatives of undecenoic acid; these two products (which have not been studied structurally) melt at 208–209°C. and 186–187°C. (8).

If ricinoleic acid and chlorosulfonic acid are allowed to react in aqueous solution for some time, or if the solution is heated, no compound is formed, but rather there results sulfuric acid and $\text{C}_{17}\text{H}_{32}\text{CO} \cdot \text{O} \cdot \text{C}_{17}\text{H}_{32}\text{COOH}$, a yellow viscous oil. On further heating there is formed a lactide of ricinoleic acid (121):



Thioindigoid dyes, probably thioindigotindithioglycolic acids, are obtained when benzene-1,2-dithioglycolic acid, benzene-1,3-dithioglycolic acid, benzene-1,4-dithioglycolic acid, 4-chlorobenzene-1,3-dithioglycolic acid, and 2,5-dichlorobenzene-1,3-dithioglycolic acid are treated with chlorosulfonic acid at 50–60°C. These dye wool and cotton with red to violet shades; they are usually better when used in an acid bath (110).

Upon condensing 1,4-benzoquinone-2,5(2,6?)-dithioglycolic acid with an excess of chlorosulfonic acid at 50–70°C. for 12 hr. there is formed a thioindigoid dye, an intensely violet substance which dyes cotton as well as wool a greenish blue color (109).

Salicylic acid, when treated with 10 parts of chlorosulfonic acid at 130–140°C. for 1.5 hr., yields the disulfonyl chloride, m.p. 185°C. (253).

One part of 1-naphthol-2,4-disulfonic acid, allowed to stand with 10 parts of chlorosulfonic acid at room temperature for 3 days, produced crystals which proved to be 1-naphthol-2,4,7-trisulfonyl chloride, m.p. 174°C. This same product was obtained after 3 hr. when the reaction mixture was cautiously poured onto crushed ice.

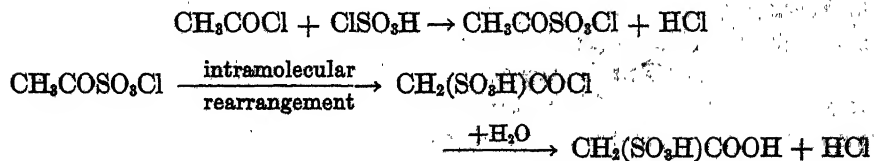
One part of the sodium salt of 1-naphthol-4,7-disulfonic acid was slowly added to 10 parts of chlorosulfonic acid; after standing for 14 days the crystals were isolated and found to be the same as above, 1-naphthol-2,4,7-trisulfonyl chloride. This compound is also obtained after a 3-hr. reaction period from 1-naphthol-4,7-disulfonic acid and chlorosulfonic acid at room temperature.

1-Naphthol-4,8-disulfonic acid, added to 10 parts of chlorosulfonic acid and heated in an oil bath for 1 hr. at 150°C., forms 1-naphthol-4,6,8-trisulfonyl chloride, m.p. 217°C.

If 1-naphthol-4,6-disulfonic acid is treated analogously at 100–150°C., and the reaction product is poured into concentrated hydrochloric acid and recrystallized from carbon disulfide, crystals are obtained which melt at 217°C. and are identical with those obtained above (108).

Chlorosulfonic acid and hydrogen sulfide react at ordinary temperatures forming sulfuric acid, hydrogen chloride, sulfonyl chloride, and sulfur (264).

(10) *Action with acid chlorides.* The reaction products of chlorosulfonic acid with the first three aliphatic acid chlorides, formed at various temperatures, were investigated by Krajčínovič (176). In the case of acetyl chloride the temperatures 20°, 45°, 60°, 100°, and 140°C. were used. One of the two sulfonic acids isolated on hydrolysis with water was found to be $\text{CH}_2(\text{SO}_3\text{H})\text{COOH}$:



At temperatures above 60°C. $\text{CH}_2(\text{SO}_3\text{H})\text{COOH}$ goes over to $\text{CH}_2(\text{SO}_2\text{H})_2$.

Above 45°C. $\text{CH}_3\text{COSO}_2\text{Cl}$ is transformed into sulfacetyl chloride, which with more chlorosulfonic acid at temperatures above 60°C. is converted into sulfomethanesulfonyl chloride, carbon dioxide, and hydrogen chloride. The substance, $\text{OC}(\text{CH}_3)=\text{CHCOCH}=\text{CCH}_2\text{COOH}$, m.p. 99°C., obtained at temperatures above 60°C., is identified as 2-methylpyrone-6-acetic acid (173).

From equal quantities of propionyl chloride and chlorosulfonic acid, allowed to stand for 5 to 10 days at room temperature and then poured into cold water, is obtained a pitch-like mass from which ether extracts α' -ethyl- β,β' -dimethylpyrone, $\text{C}_2\text{H}_5\text{C}=\text{C}(\text{CH}_3)\text{COCH}(\text{CH}_3)\text{COO}$, m.p. 151°C.; the residue remaining from the ether extract yields $\text{CH}_3\text{CH}(\text{SO}_3\text{H})\text{COOH}$. The formation of α' -ethyl- β,β' -dimethylpyrone is explained as follows: The chlorosulfonic acid combines with the propionyl chloride to form $\text{C}_2\text{H}_5\text{COOSO}_2\text{CH}(\text{CH}_3)\text{COOSO}_2\text{CH}(\text{CH}_3)\text{COCl}$; the SO_3 groups are then split off and the resulting $\text{C}_2\text{H}_5\text{COCH}(\text{CH}_3)\text{COCH}(\text{CH}_3)\text{COCl}$ partly enolizes at the δ -carbon atom, and the ring in α' -ethyl- β,β' -dimethylpyrone is closed by elimination of hydrogen chloride (174).

The action of chlorosulfonic acid on butyryl chloride at room temperature is gradual and is accompanied by a continuous evolution of hydrogen chloride and carbon monoxide. No $\text{C}_2\text{H}_5\text{CH}(\text{SO}_3\text{H})\text{COOH}$ could be obtained; extraction with ether yielded dipropyl ketone, b.p. 144°C.

The results with the three chlorides indicate that the greater the number of carbon atoms in the chloride, the fewer the number of moles that condense. Thus, 4 moles of acetyl chloride condense to form 2-methyl-1,4-pyrone-6-acetic acid, 3 moles of propionyl chloride to form α' -ethyl- β,β' -dimethylpyrone, and only 2 moles of butyryl chloride to form dipropyl ketone. The condensation products of acetyl chloride are obtained only at higher temperatures, whereas those of the other chlorides are decomposed at the higher temperatures and can be isolated only at room temperature (175). In the reaction of propionyl and butyryl chlorides with chlorosulfonic acid at ordinary temperatures carbonyl chloride groups are split off to some extent, as is shown by the continuous evolution of carbon monoxide (176).

(11) *Action with aryl halides.* When chlorobenzene and 3 parts of chlorosulfonic acid are heated for 8 hr. at 150–180°C. there is formed 2,4-(ClO_2S) $_2\text{C}_6\text{H}_3\text{Cl}$, m.p. 90–91°C. (257). Equimolar quantities of the halide and acid produce chlorobenzenesulfonic acid and a dichlorosulfo-benzide, $(\text{C}_6\text{H}_4\text{Cl})_2\text{SO}_2$ (14).

A dibromosulfo-benzide was formed when 1 mole of the halide reacted with chlorosulfonic acid; it crystallized from alcohol in long needles, melting at 172°C., and boiling without decomposition at a higher tempera-

ture. A bromobenzenesulfonic acid was also obtained (14). Under similar conditions Armstrong (5) obtained the dibromosulfobenzide, $(C_6H_4Br)_2SO_2$, which is soluble in hot alcohol, but difficultly soluble in cold alcohol; it melts at 168°C.

(12) *Action with sulfones.* Ten parts of chlorosulfonic acid heated at 150–160°C. with di-*p*-xylyl sulfone gives di(*p*-xylylsulfonyl chloride) sulfone, m.p. 190°C. (257).

Ethyl sulfone and chlorosulfonic acid heated for 6 hr. at 150–160°C. give ethyl-*m*-chlorosulfonylphenyl sulfone, m.p. 93.5°C. (257).

(13) *Action with substituted amides of cyanoacetic acid.* The following compounds were prepared by treating a substituted amide of cyanoacetic acid with an excess of chlorosulfonic acid in dry chloroform: disulfo-cyanoacetanilide, $(HO_2S)_2C(CN)CONHC_6H_5$, leaflets; the corresponding *o*-, *m*-, and *p*-toluides; the α -naphthylamide; the β -naphthylamide, yellow needles; the benzylamide, colorless plates; the xylyl (1,4,5-), colorless shining scales. These compounds are very soluble in water and almost insoluble in alcohol, chloroform, carbon disulfide, carbon tetrachloride, benzene, toluene, ether, and petroleum ether. They char when heated to 255–280°C. The reactivity of the methylene hydrogen with chlorosulfonic acid, which is absent with cyanoacetic acid, increases as phenyl, tolyl, and naphthyl radicals are substituted in the amide group, showing that the rapidity with which the reaction proceeds depends on the electronegative character of the group (228).

(14) *Action with miscellaneous reagents.* Aniline in excess of chlorosulfonic acid, heated to 150–160°C. for 2 hr. with sodium chloride, slowly reacts to give, on adding water, aniline-2,4,6-trisulfonyl chloride, m.p. 175°C. The acid chloride is obtained in only small yield if sodium chloride is absent (the free acid then being formed). *p*-Toluidine gives a 3,5-disulfonyl chloride, yellow needles, m.p. 156°C.; *m*-phenylenediamine gives the 4,6-disulfonyl chloride, m.p. 274–275°C.; *p*-phenylenediamine gives the tetrachloro derivative (189).

Benzenesulfonyl chloride, heated with 3 parts of chlorosulfonic acid for 8 hr. at 150–180°C., gives 2,4-(ClO_2S) $_2$ C $_6$ H $_3$ Cl, m.p. 90–91°C. (257).

p-Chloronitrobenzene and chlorosulfonic acid, heated for 6 to 7 hr. at 160–170°C., give 4,2- $O_2N(ClO_2S)C_6H_3Cl$, m.p. 89°C. (257).

Nitrobenzene and chlorosulfonic acid heated for 20 hr. at 150°C. give chloranil (257).

Thiophenetole and chlorosulfonic acid heated at 150–160°C. give pentachlorophenylethyl sulfide (257).

α - and β -naphthylaminesulfonates are sulfonated by chlorosulfonic acid. With the α -compound the main products are the 4- and 5-sulfonic acids, whereas the β -compound gives the 5- and 8-sulfonic acids (64).

Two moles of toluene sulphydrate to 1 mole of chlorosulfonic acid forms

p-toluene disulfide, m.p. 43°C., together with sulfur dioxide and hydrogen chloride (14).

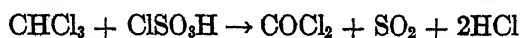
Methyl chlorocarbonate, when poured gradually into chlorosulfonic acid, forms methyl chlorosulfonate, b.p. 31°C. at 12 mm. (172).

Phenyldichloroarsine reacts with chlorosulfonic acid forming benzene-sulfonyl chloride (32).

Dewar and Cranston (52) observed that chlorosulfonic acid reacts with carbon disulfide in a sealed tube at 100°C. as follows:



In a sealed tube at 120°C. chloroform reacts with the acid as follows:



p-Tolyl acetate and 5 parts of chlorosulfonic acid were allowed to stand for 6 days at 15°C.; the only definite product isolated was *p*-cresoldisulfonyl chloride, pale yellow plates, m.p. 105°C. (115).

Aceto-*p*-toluidine in 5 moles of chlorosulfonic acid at 80°C. for 1 hr. gives aceto-*p*-toluidine-2-sulfonyl chloride, colorless prisms, m.p. 124–125°C. (158).

Phenacetin was gradually added to chlorosulfonic acid, the temperature being maintained at 50°C. for 1 hr.; 4-acetylaminophenetole-2-sulfonyl chloride, colorless prisms, m.p. 133°C., was obtained (158).

Aceto-*p*-xylylidine when kept in chlorosulfonic acid for 1 hr. at 80°C. formed aceto-*p*-xylylidine-6-sulfonyl chloride, colorless needles, m.p. 160°C. (158).

1,3-Dichloro-2-propanol, reacting with chlorosulfonic acid, yields β , β -dichloropropyl hydrogen sulfate, $\text{SO}_2(\text{OH})\text{OCH}(\text{CH}_2\text{Cl})_2$ (32).

Identification

Chlorosulfonic acid in the presence of powdered tellurium gives a cherry-red color; with powdered selenium a moss-green color (293).

III. TITANIUM TETRACHLORIDE, TiCl_4

Preparation

George (111) prepared titanium tetrachloride in 1825 by passing dry chlorine over heated titanium; Vigouroux and Arrivaut (344) and de Carli (72) passed chlorine over ferro-titanium heated to red heat; Friedel and Guérin (98) prepared it by heating crystals of titanous oxychloride; Ellis (88) ignited a mixture of rutile and powdered aluminum and heated the product in a current of chlorine; Hunter (148), Goerges and Stähler (119), and Oreshkin (240) heated titanium carbide in a stream of chlorine;

Friedel and Guérin (98) and Pamfilov and Shtandel (246) passed chlorine over heated titanium dioxide; Dumas (84) passed chlorine over a red-hot mixture of titanium dioxide and carbon. Pierre (251), Demoly (76), von der Pfordten (345), Merz (204), Oreshkin (240), and Wagner (347) also used the chlorine-carbon process, as did McInerny, Williams, and Glaze (198), who obtained U. S. patent 1,888,996 (November 29, 1932) for the process. Watts and Bell (353) passed carbon tetrachloride, chloroform, or a mixture of chlorine and carbon monoxide over red-hot titanium dioxide; Priesz (262) used chloroform as the chlorinating agent with a little carbon mixed with the titanium dioxide. Demarçay (75) found the action of carbon tetrachloride on titanium dioxide very fast at 440°C. and considered this to be one of the most convenient methods of preparation. Bourion (42) prepared the tetrachloride by the action of the vapor of sulfur monochloride and chlorine on red-hot titanium dioxide. Beloglazov (19) made briquets from ground titanium ore mixed with carbon and a binder such as starch paste and then chlorinated the briquets. Favre (93) obtained French patent 800,688 (July 16, 1936) for the preparation of the tetrachloride by chlorinating a mixture of titanium, copper, and iron; Nakrav (229) obtained Hungarian patent 115,530 (December 1, 1936) for its preparation by chlorinating material containing titanium and iron; Société des Produits Chimiques de Saint-Bueil (312) obtained British patent 458,892 (December 29, 1936) for its preparation by chlorinating titanium-iron-copper mixtures above 150°C.; Barton (6) obtained U. S. patent 1,179,394 (April 18, 1915) for the preparation of the tetrachloride by heating a mixture of titanium dioxide and soft coal until the volatilizable constituents were driven off and then treating the remaining cinder with chlorine at a temperature of 650°C.

Physical properties

Titanium tetrachloride is a transparent, colorless, mobile liquid. Its boiling point has been reported as follows: 134.8°C. at 735 mm. (89); 135.0°C. at 760 mm. (85, 130, 167, 273); 135.6–135.8°C. at 758 mm. (142); 136.0°C. at 750 mm. (39); 136.0°C. at 753 mm. (105); 136.0°C. at 760 mm. (88, 119, 344); 136.0°C. at 762.3 mm. (25); 136.4°C. at 760 mm. (334); 136.5°C. at 760 mm. (148). The following values have been given for its melting point: -23°C. (31, 89); -25°C. (132); -30°C. (181).

Titanium tetrachloride has a vapor pressure of 10.05 mm. at 20°C., 16.70 mm. at 30°C., 26.50 mm. at 40°C., 41.15 mm. at 50°C., 62.15 mm. at 60°C., 92.05 mm. at 70°C., 134.00 mm. at 80°C., 190.65 mm. at 90°C., 264.55 mm. at 100°C., 367.15 mm. at 110°C., 493.80 mm. at 120°C., 652.30 mm. at 130°C., and 740.75 mm. at 135°C. (4). Its critical temperature was estimated by Guldberg (127) as 358°C. Its vapor density is

6.836 (air = 1) or 197.4 (oxygen = 16), while the theoretical value is 190 (oxygen = 16) (84). The specific heat of the liquid between 13°C. and 99°C. is 0.18812; the specific heat of the vapor at constant pressure between 163°C. and 271°C. is 0.12897 (271). Regnault (271) determined the heat of fusion at 25°C. as 11.77 cal. per gram; Nasu (231) calculated it from freezing point data of dilute solutions as 12.90 cal. per gram. Its heat of solution is given as 59.03 Cal. (38) or 57.866 Cal. (331). Its heat of neutralization (TiCl_4 aq., 4NaOH aq.) is 47.664 Cal. (331). Its heat of formation (TiO_2 aq., 4HCl aq.) is 7.296 Cal. (331). The molecular heat of vaporization of titanium tetrachloride, calculated by the Clausius-Clapeyron equation, is 8960 Cal. for 25°C. and 8620 Cal. at the boiling point (4). The critical solution temperature of TiCl_4 - SO_2 was found to be 11.9°C. (39). Biltz and Meinecke (31) gave for the freezing point of the mixture of chlorine and titanium tetrachloride the value $-22.5^\circ\text{C}.$; the eutectic is at $-108^\circ\text{C}.$ and at a chlorine concentration of 87.5 per cent. Hildebrand and Carter (142) determined the compressibility at 25°C. to be 898 reciprocal atm. and the thermal pressure coefficient (atm. \times liters² per mole of liquid) to be 41.90. Bergmann and Engel (22) determined from the dipole moment ($\text{TiCl}_4 = 0$) and from the spatial structure that titanium tetrachloride is a regular tetrahedron.

The specific gravity of titanium tetrachloride is as follows: 1.5222 at its boiling point (334), 1.744 at 10.5°C. (118), 1.76041 at $0^\circ/4^\circ$ (334), 1.76098 at $0^\circ/4^\circ$, 1.761 at 18°C. (325), and 1.76139 at 0°C. (292). Values of its density have been reported as follows: $d_4^{15.5^\circ}$, 1.742; $d_4^{26^\circ}$, 1.725; $d_4^{40^\circ}$, 1.701; $d_4^{58.5^\circ}$, 1.673 (105). Its parachor is 262.5 (105). Its viscosity coefficient is 0.007921 at 20°C. and 0.007458 at 25°C. expressed in c.g.s. units (292). Its entropy is 59.51 at 25°C. (271). The values of its index of refraction are as follows: $n_A = 1.5651$; $n_D = 1.6039$; $n_F = 1.6296$; $n_H = 1.6814$ (118). Its molecular refraction is 65.20 (118). Its molecular dispersion is 10.74 (118). Its dielectric constant is 2.73 at 24°C. (196).

Ingersoll (152) found the magnetic rotation of titanium tetrachloride in a concentrated solution of ferric chloride to be nearly proportional to $\lambda/3$; in a solution of potassium ferrocyanide it is almost proportional to $\lambda/5$. Arai (4) found Trouton's constant to be 21.07, which shows that the tetrachloride is a normal liquid. Sulfur dioxide forms with titanium tetrachloride mixtures which are but partly miscible at low temperatures (39). Vaidyanathan (341) showed that titanium tetrachloride has a tetrahedral symmetry and gave the specific susceptibility at 35°C. the value of -0.287×10^{-6} .

Chemical properties

(1) *Action with water.* von Kowalewsky (171) showed that titanium tetrachloride dissolves in water with the evolution of much heat, and that

the hydrogen chloride liberated during the hydrolysis suffices to redissolve the precipitated hydroxide first formed without any corresponding change in the electrical conductivity. The value of the electrical conductivity shows that equilibrium is established before the hydrolysis is complete; the hydrolysis is completed by boiling, or by heating in a sealed tube at 150°C. König and von der Pfordten (169) found that with water titanium tetrachloride forms a series of oxychlorides: TiCl_3OH , $\text{TiCl}_2(\text{OH})_2$, $\text{TiCl}_2(\text{OH})_3$; with excess of water it forms $\text{Ti}(\text{OH})_4$. Wagner (347) found that when titanium tetrachloride is dropped into water, a turbid liquid is produced, but that a clear solution of orthotitanic acid in the tetrachloride can be obtained by adding water drop by drop to the tetrachloride with constant agitation. The tetrachloride emits dense white fumes in air but, according to Pierre (251), although this occurs at ordinary temperature the fuming does not occur below 0°C. The possible use of the fumes for production of clouds in modern warfare has been discussed by Richter (275) and Walker (349).

(2) *Action with metals.* Parravano and Mazzetti (248) found that at 900°C. titanium tetrachloride is reduced by iron, forming a titanide; at about 110°C. the tetrachloride is reduced by potassium to the dichloride and partly to titanium (346). Stähler and Bachran (314) showed that the tetrachloride is reduced to the trichloride by heating it with finely powdered aluminum, antimony, arsenic, or tin in a sealed tube at 400°C. Sodium amalgam reduces the tetrachloride to the dichloride (289), and at slightly elevated temperatures aluminum, magnesium, zinc, mercury, arsenic, and tin reduce it to the trichloride (289).

(3) *Action with hydrogen.* Titanium tetrachloride is reduced by hydrogen above 600°C., forming the tri- and di-chlorides (300); at red heat Goerges and Stähler (119) found that some titanium was produced. Friedel and Guérin (98) produced titanous oxychloride by passing a mixture of hydrogen and the vapor of titanium tetrachloride over white-hot titanium dioxide.

(4) *Action with ammonia and phosphine.* Rose (279) found that dry ammonia is rapidly absorbed by titanium tetrachloride with great evolution of heat; the analysis of the brownish-red product corresponds with titanium tetraamminotetrachloride, $\text{TiCl}_4 \cdot 4\text{NH}_3$; Persoz (249) obtained a pale yellow powder by Rose's process and the analysis corresponded with titanium hexamminotetrachloride, $\text{TiCl}_4 \cdot 6\text{NH}_3$; Stähler and Wirthwein (315) also obtained this compound as a saffron-yellow powder by passing the vapor of titanium tetrachloride in a stream of dried hydrogen into ammonia; Rosenheim and Schutte (280) obtained the hexamine as a dark yellow powder by passing dry ammonia into a dry ethereal solution of titanium tetrachloride cooled with ice. According to Stähler and Wirthwein (315), titanium octamminotetrachloride, $\text{TiCl}_4 \cdot 8\text{NH}_3$, is ob-

tained as a pale yellow powder when titanium tetrachloride is shaken with liquid ammonia for 12 hr.

Rose (279) showed that titanium tetrachloride absorbs phosphine, forming a brown solid, titanium phosphinotetrachloride, which, when heated in a closed vessel, forms hydrogen chloride, phosphine, and a lemon-yellow sublimate of phosphonium chlorotitanate, $3\text{TiCl}_4 \cdot 2\text{PH}_4\text{Cl}$. Høltje (146) produced $\text{TiCl}_4 \cdot \text{PH}_3$ and $\text{TiCl}_4 \cdot 2\text{PH}_3$ by the action of phosphine on titanium tetrachloride; both are yellow in color.

(5) *Action with hydrogen sulfide.* Ebelmen (86) has reported that, in the cold, hydrogen sulfide reduces titanium tetrachloride to the dichloride; at a higher temperature titanium disulfide is formed. Biltz and Keenels (30) found that dry liquid hydrogen sulfide does not react with or dissolve titanium tetrachloride, but at a higher temperature there is formed a monosulfohydrate, $\text{TiCl}_4 \cdot \text{H}_2\text{S}$, and a disulfohydrate, $\text{TiCl}_4 \cdot 2\text{H}_2\text{S}$, with the respective heats of formation 8.86 Cal. and 8.18 Cal.

(6) *Action with cyanides.* Wöhler (366) and Schneider (302) obtained the addition products $\text{TiCl}_4 \cdot 2\text{HCN}$ and $\text{TiCl}_4 \cdot \text{CNCl}$. Oberhauser (234) obtained the compound $3\text{TiCl}_4 \cdot 2\text{BrCN}$ from the tetrachloride and cyanogen bromide. Karantassis (162) prepared the addition product $\text{TiCl}_4 \cdot 2\text{HCN}$ by adding hydrogen cyanide to titanium tetrachloride in a U-tube cooled with ice and salt.

(7) *Action with oxygen and nitrogen.* A white solid of the composition $\text{Ti}_2\text{O}_3\text{Cl}_2$ was obtained by passing a mixture of oxygen and the vapor of titanium tetrachloride through a red-hot porcelain tube packed with porcelain pieces (339). When titanium tetrachloride is vaporized in a current of nitrogen and passed through the silent electric discharge at 4500 volts there is produced a compound having the formula $\text{TiNC} \cdot \text{TiCl}_4$ (143).

(8) *Action with hydrogen halides.* Ruff and Ipsen (288) obtained a citron-yellow titanium fluochloride, approximately TiClF_3 , by the action of the tetrachloride on hydrogen or silver fluoride. Hautefeuille (135) found that boiling titanium tetrachloride reacts with hydrogen iodide, forming titanium tetraiodide.

(9) *Action with phosphorus chlorides.* Bertrand (25) observed that phosphorus trichloride unites directly with titanium tetrachloride, forming yellow crystals of titanium phosphorus heptachloride, $\text{TiCl}_4 \cdot \text{PCl}_3$; Weber (355) obtained titanium phosphoric chloride, $\text{TiCl}_4 \cdot \text{POCl}_3$, by saturating a mixture of phosphorus trichloride and titanium tetrachloride with dry chlorine, and Wehrlin and Giraud (356) obtained it by heating equimolar proportions of the constituents in a sealed tube to 150°C . Weber (355) prepared titanium phosphoryl heptachloride, $\text{TiCl}_4 \cdot \text{POCl}_3$, by dropping phosphoryl chloride into titanium tetrachloride.

(10) *Action with ether and alcohol.* The compound $\text{TiCl}_4 \cdot (\text{C}_2\text{H}_5)_2\text{O}$

was obtained from the constituents (15, 25, 76, 88, 345). Demarçay (75) found that alcohol reacts with titanium tetrachloride giving crystals of $\text{Ti}(\text{OC}_2\text{H}_5)_3\text{Cl}\cdot\text{HCl}$, and that this reacts with sodium ethylate, forming ethyl orthotitanate, $\text{Ti}(\text{OC}_2\text{H}_5)_4$. Benrath (20) found that titanium tetrachloride in the presence of alcohol is slowly reduced on exposure to light; Benrath and Obladen (21) found that the photochemical reaction is accompanied by autooxidation and formation of hydrogen peroxide.

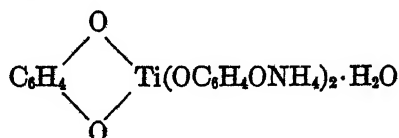
(11) *Action with acids.* Demoly (76) evaporated a strongly acid solution of titanium tetrachloride and obtained very hygroscopic crystals of the pentahydrate, $\text{TiCl}_4\cdot 5\text{H}_2\text{O}$; *in vacuo*, over concentrated sulfuric acid, the dihydrated compound $\text{TiCl}_4\cdot 2\text{H}_2\text{O}$, results. Benrath (20) showed that titanium tetrachloride in the presence of oxalic, mandelic, or lactic acids is slowly reduced in light. König and von der Pfordten (169) obtained, by regulating the mixing of concentrated hydrochloric acid with titanium tetrachloride, the three intermediate stages of hydrolysis of the tetrachloride: the first stage represented by titanium hydroxytrichloride, $\text{Ti}(\text{OH})\text{Cl}_3$, the second by titanium dihydroxydichloride, $\text{Ti}(\text{OH})_2\text{Cl}_2$, the third or penultimate stage represented by titanium trihydroxychloride, $\text{Ti}(\text{OH})_3\text{Cl}$. Weber (355) passed the dried vapors from aqua regia over titanium tetrachloride and obtained titanium dinitrosyl hexachloride, $\text{TiCl}_4\cdot 2\text{NOCl}$. Hampe (183) obtained the same product by the action of hyponitrous acid on the tetrachloride. Clausnizer (59) obtained titanium sulfatotetrachloride, $\text{TiCl}_4\cdot \text{SO}_3$, by dropping chlorosulfonic acid into titanium tetrachloride. Rosenheim, Schnabel, and Bilecki (281) prepared the compound $\text{TiCl}(\text{OC}_6\text{H}_4\text{COOH})_3\cdot \text{HCl}$ by boiling 3 moles of salicylic acid in absolute ether with titanium tetrachloride; the product formed purple-red crystals, melting at 115°C . (decomposition). Dermer and Fernelius (77) prepared the compound $\text{Cl}_2\text{Ti}[\text{OC}_6\text{H}_2(\text{NO}_2)_3]_2$ by the reaction of picric acid with titanium tetrachloride.

(12) *Action with ketones.* Dilthey (82) made substitution products of titanium tetrachloride with acetylmethylacetone, triacetylmethylacetyl-titanium titanichloride, $[\text{Ti}\{\text{OC}(\text{CH}_3)=\text{C}(\text{CH}_3)(\text{CH}_3\text{CO})\}_3\text{Cl}]_2\cdot \text{TiCl}_4$. Evard (91) and Scagliarini and Tartarni (297) prepared the compound $\text{Ph}_2\text{CO}\cdot \text{TiCl}_4$, a clear yellow, crystalline mass, by precipitating benzophenone in anhydrous benzene with a benzene solution of titanium tetrachloride.

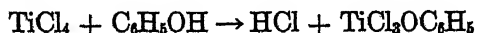
(13) *Action with acetyl- β -glucosides.* Tetraacetyl- β -hexylglucoside (m.p. 51.5°C .) in chloroform, when treated with a chloroform solution of titanium tetrachloride and boiled for 75 min. on a water bath, gives the α -isomer (m.p. 61°C .) (242); tetraacetyl- β -cyclohexylglucoside (m.p. 120 – 121°C .) in chloroform, treated with a chloroform solution of titanium tetrachloride for 75 min., gives the α -isomer (m.p. 40 – 41°C .) (243); heptaacetyl- β -methyl-

cellobioside in chloroform, heated for 6 hr. with a chloroform solution of titanium tetrachloride, yields the α -isomer (m.p. 185°C.) (244); an absolute chloroform solution of titanium tetrachloride, added to a similar solution of ethyl tetraacetyl- β -D-glucosidoglycolate, refluxed for 2.5 hr., cooled, and poured into ice water, produces acetochloroglucose, m.p. 71.5–72.5°C. (274).

(14) *Miscellaneous reactions.* Davis (70) reported that titanium-nitrogensulfotrichloride, $2\text{TiCl}_3 \cdot \text{N}_4\text{S}_4$, is formed in orange crystals when titanium tetrachloride is added to a solution of nitrogen sulfide in chloroform. Wölbling (367) obtained titaniumnitrogensulfotetrachloride, $\text{TiCl}_4 \cdot \text{N}_4\text{S}_4$, by the interaction of the components dissolved in carbon tetrachloride. Ruff (285) reported the formation of titanium sulfooctochloride, $\text{TiCl}_4 \cdot \text{SCl}_4$, by dropping acid sulfur chloride into a solution of titanium tetrachloride in sulfuryl chloride. Weber (355) obtained titanium selenium dioxyoctochloride, $\text{TiCl}_4 \cdot 2\text{SeOCl}_2$, by dropping selenium oxydichloride into titanium tetrachloride. Rosenheim and Sorge (282), upon the addition of 3 moles of pyrocatechol to an ether solution of 1 mole of titanium tetrachloride, obtained a deliquescent, non-homogeneous product which, on evaporating off the ether and rendering neutral with ammonia, gave the ammonium salt



Kashtanov (163) prepared trimethylmethane by treating a benzene solution of diphenylethoxymethane with titanium tetrachloride. 5-Chloro-2-furyl ethyl ketone (m.p. 55°C.) was prepared by Gilman, Burtner, Calloway, and Turck (117) by treating 2-nitrofuran and propionyl chloride with titanium tetrachloride. Titanium tetrachloride reacts with phenol as follows:



The trichlorotitanium phenolate obtained can be hydrolyzed thus:



Colorimetric investigations of the trichlorotitanium phenolate solution show that selective light absorption by this solution follows the Lambert-Beer law. The reaction can be used as a basis for colorimetric determination of either titanium tetrachloride or phenol (187). Titanium tetrachloride is a catalyst in the polymerization of cyclopentadiene (316). Addition of titanium tetrachloride in chloroform to chloroform solutions

of heliotropin and methyl phthalate precipitates the following crystalline addition compounds: $\text{TiCl}_4 \cdot \text{C}_6\text{H}_4(\text{COOCH}_3)_2$, bright yellow, unstable in moist air, and $\text{TiCl}_4 \cdot 2\text{C}_6\text{H}_3(\text{CHO})\text{OCH}_2\text{O}$, bright red, very unstable, fuming in air (297).

IV. SILICON TETRACHLORIDE, SiCl_4

Preparation

Silicon tetrachloride was first prepared by Berzelius (26) in 1823 by the direct union of the elements. It was later prepared by Oersted (236), Buff and Wöhler (47), Ebelmen (87), Schnitzler (303), and Baxter, Weatherill, and Holmes (11) by passing chlorine over an intimate mixture of silicon and charcoal at red heat. Brallier (43) prepared it by passing chlorine over a mixture of silicon and silicon carbide; Hempel and von Haasy (137) by treating sulfosilicates with chlorine; Robinson and Smith (277), Warren (352), de Carli (72), and Martin (192) by passing chlorine over heated ferrosilicon; Gattermann (106) used magnesium silicide; Rauter (270) used copper silicide; Hutchins (150) used silicon carbide; Vigouroux (342) used aluminum silicide. Weber (354) prepared it by heating silicochloroform with chlorine. Stock, Somieski, and Wintgen (326) found that disiloxane and chlorine react vigorously at -125°C ., forming tetrachloromonosilane.

Deville (78) showed that hydrogen chloride might be employed in place of chlorine but that the temperature would have to be higher; Currie (66) made the same observation. Faure (92) obtained silicon tetrachloride by passing a mixture of hydrogen chloride and a hydrocarbon over red-hot silica. Stock and Zeidler (327) prepared it by treating cupric silicide with hydrogen chloride at 300°C . Montemartin and Losana (222) found that, upon heating mixtures of aluminum and potassium silicates with carbon at high temperatures in a current of nitrogen, a cyanide was formed which, when heated to about 1000°C . in a current of dry gaseous hydrogen chloride, produced silicon tetrachloride.

Weber (354) and Daubrée (68), by strongly heating amorphous silica, powdered quartz, or a powdered silicate in the vapor of phosphorus pentachloride, obtained silicon tetrachloride. Didier (81) prepared silicon tetrachloride by heating cerium trichloride and silica in the presence of a weak oxidizing agent; Matignon and Bourion (194) by passing a mixture of chlorine and the vapor of sulfur chloride over silica at 450°C .; Baudrimont (7) by heating a mixture of potassium chlorate and silica above 360°C .; Friedel and Ladenburg (99), Buff and Wöhler (47), and Stock and Zeidler (327) by decomposing silicochloroform by heat; Stokes (328) by the reaction of the aromatic silicon esters with phosphorus oxychloride;

Colson (61) by reacting mercuric chloride with silicon sulfide; Budnikov and Shilov (45) by the action of sulfur monochloride on silica at 1000°C. and (46) by passing a stream of phosgene over powdered silica at 900–1000°C.

Hutchins (149, 151) obtained Canadian patent 184,354 (May 14, 1918) and U. S. patent 1,271,713 (July 9, 1918) for the preparation of silicon tetrachloride by passing dry chlorine over silicon carbide heated to almost 1000°C., and Moore (224) obtained U. S. patent 1,350,932 (August 24, 1920) for a process differing only in detail. Jüngst and Mews (160) obtained German patent 157,615 for the preparation of silicon tetrachloride by heating metal chlorides with silicon. The consortium fur Electrochemische Industrie-Ges. (62) obtained British patent 176,811 (March 13, 1922) for the preparation of silicon tetrachloride by passing chlorine, containing sulfur monochloride, over a heated mixture of silica and carbon.

Physical properties

Silicon tetrachloride is a transparent, colorless liquid, which fumes at ordinary temperatures. Berzelius (26) stated that the liquid evaporates as a white cloud, leaving a residue of silica. The vapor has a suffocating odor and reddens litmus paper.

The boiling point of silicon tetrachloride has been reported as follows: 50°C. (309); 56.8°C. (326, 365); 56.8°C. at 751 mm. (40); 56.81°C. (272); 56.9°C. (12); 57°C. (165); 57.02–57.05°C. (277); 57.50–57.55°C. at 755 mm. (142); 57.57°C. at 769 mm. (12); 58°C. (11, 131); 58.0–58.5°C. at 765.33 mm. (333); 59°C. at 766 mm. (83, 194, 251). Its melting point has been reported as –68.7°C. (326), –69.7°C. (40), –70°C. (181), –89°C. (12), and –102°C. (270).

The specific gravity of silicon tetrachloride is 1.1929 at 99.9°C. (203), 1.47556 at 22°C. (1), 1.481245 at 20°C. (277), 1.4878 at 20°C. (131), 1.4928 at 15°C. (203), 1.4933 at 15°C. (287), 1.50068 at 10.98°C. (203), 1.522 (97), 1.52371 at 0°C. (251), 1.524 at 16°C. (325), 1.52408 at 4°C. (333), and 1.54 (170). Its vapor density has been reported as 5.939 (83), 5.86 (observed) and 5.868 (calculated) (272). The values found for its surface tension were: 16.31 dynes per centimeter at 18.9°C., 13.66 dynes per centimeter at 45.5°C. (269), and 19.70 dynes per centimeter at 20°C. (219). Its specific cohesion is 2.24 sq. mm. at 18.9°C. and 1.95 sq. mm. at 45.5°C. (269). Its vapor pressure has been reported as follows: 11.6 mm. at 0°C., 13.3 cm. at 5°C., 15.0 cm. at 10°C., 17.5 cm. at 15°C., 21.6 cm. at 20°C., 26.1 cm. at 25°C., 76 cm. at 56.9°C. (12), 1.966 cm. at –25°C., 4.646 cm. at –10°C., 7.802 cm. at 0°C., 12.59 cm. at 10°C., 29.499 cm. at 30°C., 60.746 cm. at 50°C., 83.723 cm. at 60°C., 97.274 cm. at 65°C. (272), 77 mm. at 0°C., 98 mm. at 5°C., 124 mm. at 10°C., 153 mm.

at 15°C., 191 mm. at 20°C., 235 mm. at 25°C., 287 mm. at 30°C., 346 mm. at 35°C., 419 mm. at 40°C., 501 mm. at 45°C., 599 mm. at 50°C., 709 mm. at 55°C., 839 mm. at 60°C. (165), 238.3 mm. at 25°C. (368). Its critical temperature is 213.8°C. (269), 221°C. (128), 230°C. (203), 233.6°C. (247).

The heat of fusion of silicon tetrachloride is 10.85 cal. per gram at -70.3°C. (181). Its heat of vaporization is 6.3 Cal. per mole (238) or 7.19 Cal. per mole (326). Its heat of formation is as follows (24, 338):



The calculated value in the latter case is 154 Cal. (283). The temperatures of formation of silicon tetrachloride from silicon dioxide, chlorine, and carbon are 740°C. from amorphous silicon dioxide, 1060°C. from tridymite or cristobalite, and 1220°C. from quartz (122).

The coefficient of thermal expansion of silicon tetrachloride at 20°C. is 0.001430 (251) or 0.001446 (333); between 25° and 30°C. it is 0.0014124 (277). Its specific heat is 0.1904 between 10° and 15°C. (238, 272), 0.1904 between 20° and 40°C. (161), 0.1322 between 90° and 234°C. (272). Its index of refraction has been reported as follows: 1.404 for red light (107); H_{α} , 1.4119 (red ray); H_{β} , 1.4200 (green ray); H_{γ} , 1.4244 (violet ray) (131); 1.41019 for the H_{α} -ray; 1.41829 for the H_{β} -ray; 1.41257 for the D-ray; 1.42306 for the H_{γ} -ray (1). For rays of wave length $\lambda = 226, 394$, and $589 \mu\mu$, the index of refraction = 1.50823, 1.43334, and 1.4182, respectively (325). The beginning of continuous absorption in the spectra of the hot vapors was determined as λ 2500 for silicon tetrachloride (71). Bergmann and Engel (22) determined from the dipole moment ($\text{SiCl}_4 = 0$) and from the spatial structure that silicon tetrachloride is a regular tetrahedron. The dielectric constant was found to be 2.40 by Schundt (305) at 16°C. with wave length $\lambda = 80$ cm. Schuster (306), by the use of an equation derived from Stefan's equation and the Clausius-Clapeyron equation, calculated the internal pressure of silicon tetrachloride as 1184. The solubility of iodine in silicon tetrachloride, expressed as mole per cent, is 0.1713 at 0.10°C., 0.4987 at 25°C., and 0.8801 at 40°C. (232). Biltz and Keunecke (30) found that anhydrous liquid hydrogen sulfide at -78.5°C. dissolves silicon tetrachloride without discontinuity in the isothermal vaporization curve. Wood (368) determined the fugacity of silicon tetrachloride as 234.5 at 25°C. Taylor and Hildebrand (330) found that at 0°C. 0.131 g. of chlorine dissolves in 1 g. of silicon tetrachloride. Biltz and Meinecke (31) found the freezing point curves of mixtures of silicon tetrachloride and chlorine to have a eutectic at -117°C. with 86 per cent of chlorine. Besson (28) observed that silicon tetrachloride does not absorb phosphine at ordinary temperature, but that it dissolves twenty

times its volume at -20°C . and forty times its volume at -50°C . The conduction of a saturated solution of silicon tetrachloride in liquid hydrogen sulfide = $0.129 (\lambda \times 10^6)$ (268). The compressibility of silicon tetrachloride in reciprocal atmospheres at 25°C . is 1652 (142). Its thermal pressure coefficient (atm. \times liters² per mole of liquid) is 34.00 (142).

Chemical properties

(1) *Action with hydrogen and oxygen.* When a mixture of silicon tetrachloride vapor and hydrogen is heated to redness, siliconchloroform is produced (100); when a mixture of the tetrachloride vapor and dry oxygen or air is heated, an oxychloride, $2\text{Si}_2\text{OCl}_6$, is obtained (100). Troost and Hautefeuille (340) obtained the same oxychloride by passing silicon tetrachloride through a heated porcelain tube with or without a packing of fragments of feldspar or alkali silicates.

(2) *Action with water.* According to Berzelius (27) silicon tetrachloride first floats on the surface of water and then dissolves with decomposition, forming hydrated silica and hydrogen chloride. Silicon tetrachloride and water form metasilicic acid (327). At a red heat Daubr  e (69) found that water vapor and silicon tetrachloride produced crystals of silicon dioxide. Schwarz and Liede (308) obtained the α -acid by the hydrolysis of silicon tetrachloride at 100°C .

(3) *Action with ammonia, hydrazine, and sodamide.* Gaseous ammonia reacts with silicon tetrachloride alone or dissolved in benzene, forming silicontetramide (183). By saturating silicon tetrachloride with dry ammonia a white mass of silicon hexamminotetrachloride, $\text{SiCl}_4 \cdot 6\text{NH}_3$, is formed (37); upon passing gaseous ammonia into a solution of silicon tetrachloride in benzene in an atmosphere of dry nitrogen a product was obtained approximating silicon octamminotetrachloride, $\text{SiCl}_4 \cdot 8\text{NH}_3$ (183). Lay (182) found that with hydrazine a white, fuming compound, probably silicon tetrahydrazinetetrachloride, $\text{SiCl}_4 \cdot 4\text{N}_2\text{H}_4$, is formed by the action of a benzene solution of silicon tetrachloride on an emulsion of hydrazine in benzene; he also showed that the tetrachloride reacts with sodamide at 150°C ., forming silicon and a sublimate of ammonium chloride and silicon tetraamminotetrachloride.

(4) *Action with acids and acid anhydrides.* Hydrogen iodide and silicon tetrachloride vapor at a dull red heat produce a mixture of chloriodides (28). Hydrogen sulfide does not act on silicon tetrachloride at ordinary temperature, but at red heat silicon tetrahydrosulfide is formed (100, 130).

Concentrated sulfuric acid, decomposes silicon tetrachloride into silicon dioxide and hydrogen chloride (309). Chlorosulfonic acid decomposes silicon tetrachloride in the presence of sunlight or at 170°C . (60). Neither nitric acid nor aqua regia unites with silicon tetrachloride (354). Nitrous acid was found by Weber (354) to react with silicon tetrachloride to form

nitrosyl chloride. Butyric acid when heated with silicon tetrachloride in a sealed tube to 150–160°C. forms butyl chloride (270). Montonna (223) prepared chlorides of acetic, propionic, butyric, isobutyric, benzoic, phenylacetic, and sebacic acids by heating the respective acid with silicon tetrachloride.

At red heat phosphorus pentoxide reacts with silicon tetrachloride to form oxychlorides of phosphorus (100, 270). When pure melted sulfur trioxide is mixed with silicon tetrachloride, a mere solution is formed at first, but on standing a reaction takes place, very slowly in the cold and more rapidly if the mixture is heated to 50°C. This reaction produces probably a mixture of $\text{S}_2\text{O}_5\text{Cl}_2$ and Si_2OCl_6 (295). Gustavson (129) formed pyrosulfuryl chloride by the reaction of sulfur trioxide with silicon tetrachloride.

(5) *Action with halogens and halogen salts.* Moissan (221) found that arsenic trifluoride reacts in the cold with silicon tetrachloride, forming silicon tetrafluoride and arsenic trichloride. Hollemann and Slijper (145) found that sodium fluoride reacts with silicon tetrachloride, forming sodium chloride and silicon tetrafluoride.

(6) *Action with silicon and carbon.* When silicon tetrachloride vapor was passed over heated silicon Troost and Hautefeuille (340) obtained a subchloride. Ruff (286) found that silicon tetrachloride is not affected by carbon at high temperature, while Pring and Fielding (263) observed the formation of silicon carbide in the presence of hydrogen at 1700°C.

(7) *Action with metals.* When potassium is heated in the vapor of silicon tetrachloride the metal burns, forming potassium chloride and silicon; if molten potassium is dropped into liquid silicon tetrachloride an explosion results. Sodium, zinc, and silver at a red heat withdraw the chlorine from silicon tetrachloride without forming higher chlorides (18, 100); Rauter (270) found that zinc, aluminum, beryllium, and magnesium react at 200–300°C., forming the metal chloride and silicon. Parravano and Mazzetti (248) found that silicon tetrachloride reacts with iron at 900°C., forming an iron silicide. Vigouroux (343) showed that, with reduced iron at dull red heat, iron silicide and ferrous chloride are formed; cobalt and nickel react similarly.

(8) *Action with metal oxides.* Rauter (270) found that most metal oxides react with silicon tetrachloride, forming the metal chloride or oxychloride and silica. Sodium oxide reacts with silicon tetrachloride at red heat, forming sodium silicate and sodium chloride (100).

(9) *Action with salts.* At ordinary temperatures lead thiocyanate reacts with silicon tetrachloride to form silicon tetrathiocyanate (100). Montonna (223) prepared the anhydride of acetic acid by heating anhydrous sodium acetate with silicon tetrachloride.

(10) *Miscellaneous reactions.* *Pharmazeutische Industrie* and Hauschka

(25) obtained Austrian patent 86,131 for the preparation, from guaiacol and silicon tetrachloride, of dichlorodiguaiacolsilicomethane, $\text{SiCl}_2(\text{OC}_6\text{H}_4\text{OCH}_3)_2$, and tetraguaiacolsilicomethane, $\text{Si}(\text{OC}_6\text{H}_4\text{OCH}_3)_4$.

Rosenheim and Sorge (282) from an ethereal solution of 1 mole of silicon tetrachloride and 3 moles of pyrocatechol obtained a mass of very deliquescent, white crystals which gave off hydrogen chloride; from the condensed ethyl alcohol solution of these, alcoholic ammonia precipitated ammonium tripyrocatecholsilicate, $\text{C}_6\text{H}_4\text{O}=\text{Si}(\text{OC}_6\text{H}_4\text{ONH}_4)_3$, white crystals. Similarly, an alcoholic solution of pyridine gives the pyridinium salt, which forms bright yellow prisms.

By the action of silicon tetrachloride on dry acetone, Currie (66) obtained a jelly-like mass which, upon stirring with water, gave mesityl oxide.

From an ether solution of silicon tetrachloride, treated in the cold with an ethereal solution of ethylmagnesium bromide and then refluxed for 3 to 4 hr., Martin and Kipping (193) by careful fractionating obtained ethylsilicon trichloride, b.p. 100°C ., diethylsilicon dichloride, b.p. $128\text{--}130^\circ\text{C}$., and triethylsiliclyl chloride, b.p. 143°C .

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THE ELASTICITY OF LONG-CHAIN COMPOUNDS AS A STATISTICAL EFFECT

H. MARK

International Paper Company, Hawkesbury, Ontario, Canada

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I. INTRODUCTION

All substances built up of long, flexible, main-valence chains show a *high reversible elasticity* as one common property (18, 19). The range of temperature in which this phenomenon occurs may be rather wide (polyvinyl alcohol and rubber exhibit high elasticity at normal temperature, whereas other compounds as, for example, polystyrene, sulfur, etc., require higher temperatures). However, rubber-like elasticity occurs only with substances built up of long, flexible chains, which may be linked together in a flexible network. We find typical rubber-like elasticity in polyvinyl alcohol (Vinacol), polybutadiene (Buna), polydimethylbutadiene (methyl rubber), polyacrylester as well as vinyl chloride (Mipolam), muscle fibroin, polychlorobutadiene (Neoprene, Sovprene), polyethylene sulfide (Thiokol, Baerit), polyphosphonitrilic chloride, and finally in vulcanized oils (rubber substitute) as well as in elastic sulfur. At certain temperatures all these substances exhibit a reversible elastic limit up to at least 500 per cent and show a modulus of elasticity lying between $10^{5.5}$ and 10^7 dynes per square centimeter. In the investigations of rubber, Buna, Mipolam, methyl rubber, and rubber substitute, it was found that the modulus of elasticity increases proportionally with the absolute temperature. The fact that heat is generated during elongation stands in direct contrast to the behavior of normal elastic bodies as, for example, aluminum, steel, quartz, glass, etc.

It is very remarkable that substances of such different chemical character exhibit such similar mechanical properties. One is induced to explain this behavior on the basis of their having the same principle of molecular structure. In fact, all the materials mentioned consist of long, chain-like molecules of a certain degree of flexibility, the number of the chain links varying between 100 and 1000. The flexibility is the result of the free, or nearly free, rotation of the units round the normal carbon linkage.

II. THE FREE ROTATION

This principle of free rotation, detected long ago by the organic chemists, is necessary to explain that a great number of isomers never could be

¹ Revised in proof.

isolated. This principle has been very useful in discussing racemizations and isomerizations of different kinds. Recently it received quantitative support in the experimental work of Eucken and his collaborators (4), as well as in the theoretical considerations of Eyring (5).

We know that at normal temperature the two CH_3 - groups in the molecule of ethane rotate freely, because the normal thermal movement is sufficient to overcome the energy level that separates the different stable arrangements of the molecule. Eyring, Hückel, Pauling, and Slater have shown that a quantum-mechanical treatment of the single carbon-carbon bond explains the free rotation fairly well. On the other hand, experiment and theory agree that the double carbon-carbon linkage is rigid and defines a certain plane; this is characteristic for the structure of the molecule containing the double bond.

If one introduces substituents into ethane a certain hindrance of the free rotation results, which may lead to the formation of different stable arrangements. This intramolecular steric hindrance decreases with increasing temperature, because an increase of the vibratory and rotary motion of the different parts of a molecule tends to reproduce the free rotation (15).

Many investigations concerning the form of paraffin chains in the gaseous and in the dissolved state show that unbranched and unsubstituted hydrocarbon chains show free, or nearly free, rotation at normal temperature, and that even after substitution with groups of medium size the mobility of the molecule is maintained to a certain degree. Only if many large substituents are incorporated into the chain does the free rotation decrease remarkably. This is connected with the behavior of many main-valence chains, which also have long thread-like molecules but do not exhibit rubber-like elasticity. Carothers (2), Staudinger (25), and others have shown that polystyrene, polyindene, etc., are built up of long chains without rubber-like elasticity at normal temperatures. At higher temperatures elasticity can be observed. This is due to the fact that the steric hindrance of the rather large groups decreases with increasing thermal motion. Similarly, many cellulose derivatives do not show rubber-like elasticity, although they are built up of long chains. This is due to the fact that the ring structure of the glucosidic residue and of the 1,4-glucosidic linkage as detected by W. N. Haworth does not produce enough internal mobility for these substances at room temperature. They all have a certain rubber-like elasticity at higher temperatures.

Summarizing, we may state that rubber-like elasticity will always be observed if the presence of long-chain molecules with sufficient *internal* mobility can be assumed.

III. THE ELONGATION OF NORMAL BODIES AND LONG-CHAIN SUBSTANCES

It also seems necessary to point out that substances that do not exhibit *both* of these qualities never have an appreciable range of reversible elongation. They are characterized by the normal elastic properties of solid bodies. Their elasticity differs very distinctly from that of rubber in the limit of extensibility and especially in the different thermoelastic behavior.

We are rather well informed as to the mechanism of elastic elongation of crystals. The elementary particles of the substance—atoms, ions, or molecules—are arranged in equilibrium positions and perform small, nearly elastic oscillations around the minimum points of the potential energy; the vibrations increase with rising temperature. If one stresses such a body, then the elementary particles are moved out of their equilibrium positions and vibrate around a new minimum of potential energy, the distance of which is slightly larger than before and the energy level of which is increased. The increase in distance represents the elongation of the substance; the increase of the energy level of the equilibrium position means that now a certain amount of elastic energy is contained in the sample.

When the stress ceases, then the elementary particles return to their original positions and lose their excess of energy. The normal state is reproduced entirely. According to thermodynamics the substance must cool off during rapid elongation and heat up during rapid relaxation. Experiments confirm this postulate and show that normal solid bodies—diamond, quartz, platinum, etc.—show for their elastic elongation a range lying between 10^{-2} and 1 per cent. The modulus of elasticity is of the order of magnitude of 10^{10} to 10^{12} dynes per square centimeter and decreases with increasing temperature.

Quite different behavior is exhibited by all rubber-like substances. The limit of reversible elastic extension amounts to 1000 per cent and more; the elongation curve generally starts linear from the point of origin but afterwards exhibits a very complicated behavior; the modulus of elasticity is not at all constant during elastic extension.

Figure 1 shows a characteristic elongation curve of rubber of a low degree of vulcanization, the modulus of which lies at the beginning of the elongation between 10^5 and 10^7 dynes per square centimeter. It is much lower than for crystallized substances. During rapid elongation the substance evolves heat and during rapid relaxation it cools down (7, 12, 15, 16, 18, 19, 24).

If one observes the elongation of rubber by means of x-ray analysis as first reported by Katz (14), one finds a diffused halo in the unstressed state, which shows that the substance is of amorphous character. This diffuse ring was very carefully studied by Warren; it remains up to an

elongation of about 100 per cent. Later, sharp clear crystal-interference spots occur and demonstrate that during stretching an orientation of increasing degree takes place. Hauser and Mark (10), Mark and von Susich (18), Lotmar and Meyer (16), and recently especially P. A. Thiessen (27) and G. L. Clark (3) have investigated the crystal interferences and have derived from them a model for the molecular structure of natural rubber.

Other long-chain substances show a similar behavior. Carothers (2) in the case of Neoprene and Brill (1) in the case of Oppanol succeeded in detecting remarkably sharp crystal interferences during elongation. The

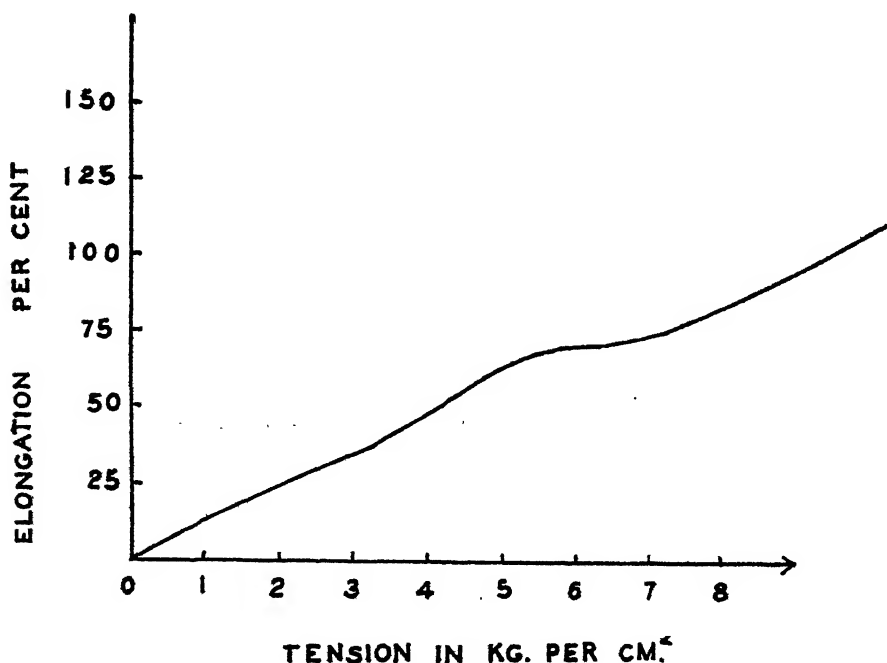


FIG. 1

modulus of elasticity and the trend of the stretching curve depend to a high degree on the temperature and on the degree of vulcanization. The typical rubber elasticity is shown only by samples that are not too highly vulcanized. If too many cross linkages are formed between the movable chains by means of sulfur bridges, the rubber-like elasticity disappears and one approaches more and more the normal behavior of crystallized solid bodies (hard rubber). The modulus of elasticity, which is calculated from the first part of the elongation curve, increases if the temperature is raised. This has been specifically demonstrated by K. H. Meyer (19) and Ornstein (21).

The enumeration of these properties shows that the molecular mechanism of the elasticity of rubber is fundamentally different from that of normal elasticity. It is very probable that the elasticity of rubber is intimately connected with the existence of flexible, long-chain molecules. Several years ago E. Wöhlisch (29) and K. H. Meyer (19), on the basis of their examination of the dependability of the modulus of elasticity on temperature, interpreted the elasticity of rubber and of proteins as a kinetic effect.

IV. THE INTRAMOLECULAR STATISTICS OF AN ISOLATED LONG-CHAIN MOLECULE

We start from a very simple example and consider first an isolated long-chain molecule, for instance, a normal hydrocarbon chain with n chain links, i.e., with $(n + 1)$ carbon atoms

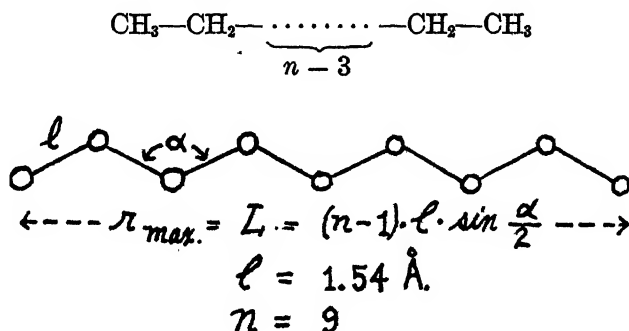


FIG. 2

the number n being of the order of magnitude between 100 and 10,000. This model is much simpler than natural rubber, because the methyl groups and the double linkages are not present, but we want to study first the behavior from the principal point of view. Later we shall have to bear in mind that there exists no real free rotation and that the different chains of a macroscopic sample mutually hinder each other.

Stereochemistry teaches that the distance x between two subsequent carbon atoms is 1.54 Å. and the angle α between two valences is about 109° . If we stretch the chain to its maximum length, as shown in figure 2, the distance between the end groups is given by

$$r_{\max.} = L = (n - 1) \cdot l \cdot \sin \frac{\alpha}{2} \quad (1)$$

One can easily see that this maximum length of the chain can be realized only in one way: namely, if all linkages lie in one plane building up the zigzag band shown in figure 2.

On the other hand, if we do not want the maximum possible distance between the first and the last carbon atom, but rather want to have a shorter distance for r ,

$$r < r_{\max.}$$

we can realize this in many different ways. Owing to the flexibility of the chain, we have ample possibilities for arrangement of its different chain links, so that the distance r between the two ends is always maintained.

For every given r a quite definite number of realizations exist, which, according to Boltzmann, can also be called the "complexions." In order to calculate these complexions as a function of r one has to make certain assumptions concerning the constitution of the chain and the mobility of its parts. When the length of one chain link is designated by l , the number by n , the angle between two subsequent links by α , and absolutely free rotation is assumed, E. Guth (8) and H. Eyring (5) have shown that the probability W that the distance between the two chain ends corresponds to r is represented by

$$W(n, l, \alpha, r) r^2 dr = 3 \sqrt{\frac{6}{\pi}} \cdot \frac{1}{n^{\frac{1}{2}} l^2} \cdot e^{-\frac{3r^2}{2nl^2}} r^2 dr \quad (2)$$

$$l^2 d = l^2 \cdot \frac{1 + \cos \alpha}{1 - \cos \alpha}$$

The equation shows that there exists a most probable distance, λ , between the chain ends: namely, the r by which the function W reaches its maximum value. This r is given by

$$\lambda = l \cdot \sqrt{\frac{2}{3}} \cdot \sqrt{n}$$

and is proportional to the square root of the chain links, as one would expect on the basis of the statistical character of the whole calculation.

Figure 3 shows W as function of r for $n = 30$. One sees that W is unsymmetrical compared with the well-known Maxwell-Boltzmann distribution curve. The distribution function is much broader than in normal statistics, owing to the fact that the number of members that are treated statistically is very much smaller than in the gas theory. As a consequence, in dealing with intramolecular statistics one has always to take seriously into account the phenomena of fluctuation, much more so than in the statistics of gaseous or solid bodies. All these considerations lead to the assumption that a chain that is in thermodynamical equilibrium with its surrounding matter will always tend to get into the condition that has the greatest number of possible realizations. This means noth-

ing else but the application of the Maxwell-Boltzmann statistics to one single macromolecule, and serious objections will not be raised as long as the number of independent elements for a statistical treatment is sufficiently large.

With this limitation we ascribe to an isolated main-valence chain an entropy, s , and calculate this entropy by the Boltzmann equation

$$s = k \ln W \quad (3)$$

W being taken from equation 2.

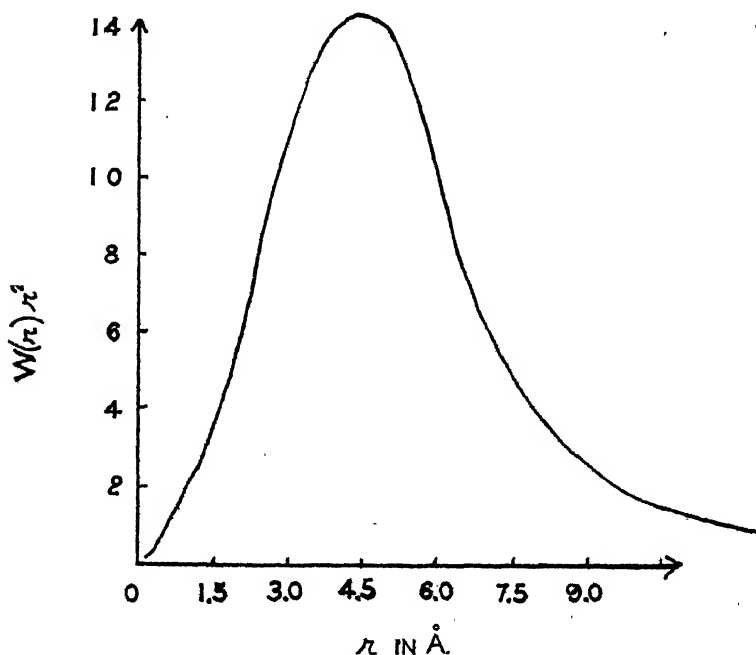


FIG. 3

First we find that such a chain will by itself always tend towards the state of greatest entropy, i.e., greatest probability. If one wants to obtain a state of smaller entropy one has to put work into the system. If we have a chain with the distance r between the end groups and want to stretch it to its maximum length, $r_{\max.} = L$, we have to put in a work A , which is equal to the difference of the entropy between the two states

$$A = S_r - S_L \quad (4)$$

During an adiabatic extension an equivalent amount of heat

$$Q = A$$

is produced. This is absolutely identical with the heating of an ideal gas during adiabatic compression. Here we obtain a loss of entropy because certain parts of the volume, which formerly were at the disposal of the gas molecules, are now blocked for them. As a consequence the number of realization possibilities and hence the probability and the entropy must decrease.

The pressure, p , of an ideal gas is exerted by the irregular motion of the molecules, which tends to increase the volume of the gas and hence to increase the number of complexions. In the same way the tension σ at the ends of a stretched main-valence chain is caused by the irregular thermal movement of the different parts, which tries to shorten the chain, because the shorter state has a greater number of possible realizations and hence a higher entropy value. In formulas:

$$p = + \left(\frac{\partial S}{\partial V} \right)_T \cdot T \quad (5)$$

$$\sigma = - \left(\frac{\partial S}{\partial (\delta l)} \right)_T \cdot T \quad (6)$$

δl = the change in the length of the chain

One can understand now why rubber-like substances show a rise in temperature during stretching and cool during relaxation, in absolute analogy to the behavior of ideal gases and in complete contradiction to normal crystal elasticity.

Ideal gases have an inner energy, U , which is independent of the volume. In the same way we can define as "ideal rubber" highly elastic substances that have an inner energy independent of elongation. Experiments carried out by E. Guth and coworkers (8, 9, 12, 22) have shown that rubber samples of a low degree of vulcanization have at about 250 per cent elongation an inner energy, which varies only very little with the stress. Real gases and rubber under other conditions show another behavior, because the forces between the different parts of a chain and the forces between different chains result in a dependence of the inner energy upon the elongation.

V. THE EQUATION OF STATE FOR THE IDEAL RUBBER

We will now, in analogy to an ideal gas, attempt to establish an equation of state for the ideal rubber. We start with equation 6. If we introduce $k \ln W$ for s and eliminate W from equation 2 we obtain:

$$\sigma = kT \cdot \frac{3}{nl^2} \cdot \frac{1 + \cos \alpha}{1 - \cos \alpha} \cdot \delta l \quad (7)$$

δl = the elongation of a single chain, just as one gets for one molecule of an ideal gas the relation

$$p = kT \cdot \frac{1}{V}$$

Therefore we seem to be justified in interpreting equation 7 as the equation of state of the ideal rubber. It combines the tension σ with the elongation δl and represents the extension curve of a single main-valence chain.

Experimentally one always measures the elongation with a macroscopic piece of rubber, which has an original length L_0 and which reaches a certain elongation δL under the influence of the stress. Therefore we must pass from formula 7 to a macroscopic piece of material.

We consider a volume unit of rubber and assume that there are Z chains contained in it. When we put the sample under a certain macroscopic tension Σ , it undergoes an elongation δL . Now, as a first approximation we make the assumption that the entropy of the macroscopic piece of rubber is given by the sum of the entropies of the single chains. This is surely only a very rough approximation, and we shall see later what change we have to make in this preliminary hypothesis.

With such assumptions we obtain:

$$\begin{aligned}\Sigma &= Z \cdot kT \cdot \frac{3}{nl^2} \cdot \frac{1 + \cos \alpha}{1 - \cos \alpha} \cdot \delta L \\ &= Z \cdot kT \cdot K \cdot \delta L\end{aligned}\tag{8}$$

$$\Sigma = E \cdot \delta L$$

$$E = kT \cdot K \cdot Z\tag{9}$$

From equation 9 one sees that the macroscopic modulus of elasticity E of rubber-like substances is proportional to the absolute temperature. This fact was proved in the range between -50° and $+80^\circ\text{C.}$ by recent experiments of K. H. Meyer (19), Ornstein (21), and their collaborators for the first part of the elongation curve. Equation 8 further shows that there is proportionality between the tension Σ and the elongation δL , a fact which is also in very good agreement with many experimental investigations of the first part of the elongation curve of rubber of a low degree of vulcanization.

A further evaluation of relation 9 was given by W. Kuhn (15). The number of chains, Z , in the volume unit is closely connected with the

average molecular weight, M , of a single chain. If ρ designates the density of the material one finds

$$Z = \frac{\rho}{M} \cdot N$$

$$E = RT \cdot K \cdot \frac{\rho}{M} \quad (10)$$

Therefore the modulus of elasticity can be used to determine the average molecular weight (M) of the single chain. If one starts from the experimental values mentioned above (10^6 to 10^7 dynes per square centimeter), one obtains for the molecular weight of the rubber chains figures between 20,000 and 100,000, which are in good agreement with other quantitative data for this substance.

Another close analogy between ideal rubber and an ideal gas, based on the similar statistical treatment, results when one compares the conditions during very slow and very rapid elongation with the slow and rapid compression of an ideal gas. If one stretches rapidly one can realize with good approximation an adiabatic process, while an isothermal process is realized when one stretches slowly. One can combine isothermal and adiabatic processes of elongation and relaxation of rubber in a Carnot-cycle process exactly as with an ideal gas, and it is easy to show that one obtains the same results as when applying the second law of thermodynamics in the usual way. It may be of interest to add that one must distinguish between the specific heat at constant length and the specific heat at constant tension exactly as one has to consider two specific heats in the case of an ideal gas. The part of the gas constant R is represented in our case by R and K .

VI. HIGHER DEGREES OF ELONGATION; TRANSITION TO THE REAL RUBBER

Although it is possible to get fairly good qualitative agreement with the properties of rubber when applying the idea of intramolecular statistics, it must be clearly pointed out that there exists so far no quantitative treatment for the behavior of a macroscopic piece of rubber during the whole range of its elastic stretch. Relation 7 only refers to the beginning of the elongation curve, during which the tension and the elongation are proportional. If one wants to go further, one must improve the equation of state of the ideal rubber in the same way as is done with the ideal gas equation by van der Waals' theory. If one wants to do this, one must consider that two kinds of corrections must be taken into account. The first of them concerns the single isolated chain, the other the interaction of different chains.

When discussing the single chain, we have so far made certain assump-

tions which surely are not right and therefore it will be necessary to give them up gradually. On the other hand, it certainly is not correct to consider a single chain in a macroscopic piece of rubber as independent of all others. Hence the required improvements can be divided into two groups: (1) The statistics of an isolated main-valence chain, which have up to now only been evaluated as a pure statistics for different positions with equal energy, have to be improved by taking the attraction and repulsion forces between the parts of a chain into account. (2) The forces between the different chains in a macroscopic piece of the substance must be discussed in a suitable way.

(1) We must point out that in regard to the van der Waals attraction and repulsion forces not all possible arrangements of a chain have the same energy. Calculating W in equation 2 we have considered them all as statistically equivalent. This certainly is not permissible. We have to proceed in another way. Every individual position of a chain has to receive a certain statistical weight, g , i.e., we have to multiply every microscopic possibility of realization for a certain given distance r between the chain ends by a Boltzmann weight factor of the form

$$g_i = e^{-\frac{u_i}{kT}}$$

and to take all these factors into account when we calculate the probability of a given (macroscopic) distance r . This would be a very complicated and nearly impossible task, and one may be induced to try some possible abbreviation. It seems reasonable to follow the ideas of van der Waals and to divide the two possible influences into (a) repulsion forces and (b) attraction forces.

As E. Guth (8) has pointed out, the *repulsion forces* can be considered in a preliminary way by something like a volume correction, exactly as was done in the theory for a real gas. In our case this means that if we want to give to our single main-valence chain a certain individual position to produce a given distance r between its ends, we begin with one end of the chain and arrange link after link in such a way that the distance between the ends becomes r . In doing this we have to be careful not to put new links in a place which is already occupied by a former part of our chain. The molecule has a certain *own volume*, which can be introduced into the formulas by replacing l in equation 2 by another quantity, l_0 .

In analogy to the van der Waals covolume b , the quantity l_0 could be called the colength of the chain. The application of this correction increases the most probable chain length, λ , and has the consequence that the distribution function of figure 3 is shifted to higher chain lengths. The particles increase in length as compared to their dimensions without this correction.

The average and the most probable shape of a given main-valence chain is a very important problem, which can not yet be entirely solved. W. Kuhn (15) has shown in a very interesting publication that one always must expect the form of a coil. But, as Guth (8) has pointed out, the calculations cannot be regarded as being quite satisfactory from a quantitative point of view. Anyhow one finds that the chains are certainly not straight, as Staudinger (25) assumes in many of his well-known contributions. They also seem not to be so much wound as is called for by the calculations of Kuhn. Experiment and, as Guth was able to show by a very interesting calculation, theoretical considerations also lead to the result that the chains are in their free state only moderately curved and wound without showing sharp angles or curvatures (8).

The forces of attraction between the different links of a single chain have been used by Fikentscher and Mark (6) and by E. Mack (17) in formulating a theory of the elasticity of rubber. The former authors emphasized that the secondary valences between the double bonds should be responsible for the attraction between the different isoprene residues and tend to shorten an extended rubber chain. E. Mack showed that more probability seems to exist for the hypothesis that the van der Waals forces between the hydrogen atoms of the hydrocarbon are responsible for this inner tension of a rubber macromolecule. In these two theories only the inner van der Waals forces of the thread-like molecules have been considered, but so far no reference has been made to the entropy of such a chain. This seems to be not justified, but one certainly has to use these forces as a correction in the same sense as the van der Waals force constant enables the treatment of a real gas.

(2) Considering the mutual interaction between the different chains it is very striking that rubber, after elongation to 100 per cent, exhibits the well-known crystal structure that was first reported by Katz and further investigated by different authors during recent years. Also, synthetic long-chain products as, for example, Neoprene and Oppanol, show similar effects. Especially in the former case W. Carothers (2), as previously mentioned, was able to observe very sharp and intensive interference spots, while R. Brill (1) obtained with samples of Oppanol at least an orientation parallel to the direction of the stress. These facts show that at higher stretches the chains arrange themselves more and more in the extended form and aggregate under the influence of the mutual attraction forces to more or less oriented bundles, which give rise to the crystal interferences, the size of which can be estimated by following the procedure of Hengstenberg and Mark (11).

The relatively short hydrocarbon chains of normal paraffins crystallize spontaneously (20). They have a small number (n) of links in every individual chain and hence (cf. equation 2) the probability of the extended or

nearly extended form, which fits in the crystal lattice, is only somewhat smaller than the one which results as most probable from statistical considerations. The natural energy and entropy fluctuations of the system are sufficient to produce straight chains to such an extent that the material crystallizes rather quickly. Therefore such substances crystallize spontaneously from solution or from the liquid phase. It fits well into this picture that the power to crystallize decreases rapidly with increasing chain length.

Truly high-polymer substances have chains which are built up of much more independent parts and their distribution function is therefore much steeper. In such cases the normal fluctuations are not sufficient to realize a frequent formation of straight or nearly straight chains. Hence the velocity of crystallization decreases more and more, and finally there is no orientation of the macromolecules at all. Only if one stretches the single chains by applying additional tension from outside and thereby increases the number of straight (less probable) individuals, does the number of these chains, which alone fit into the lattice and hence alone can undergo crystallization, become large enough and the well-known crystal interference patterns appear.

Very interesting measurements of G. von Susich (26), P. A. Thiessen and Wittstadt (27, 28), and Hauck and Neumann (9) show that at a given temperature the amount of crystallization increases with increasing tension and that at a given tension the crystals can be destroyed by increasing the temperature. As Thiessen has clearly pointed out, we have the case of an equilibrium between two phases—liquid and crystalline—which largely depends on the tension (as in other cases on the pressure).

It has been observed that when a stretched rubber band, which exhibits very distinct interference patterns, is heated, the intensity of these spots decreases with increasing temperature and at last completely vanishes. The temperature at which the x-ray interference spots disappear depends primarily on the degree of extension. However, if one has a stretched rubber band at a temperature at which interference spots are just not yet detectable and one increases the tension, then the x-ray diagram appears. This means that the intensity of the interference lines, i.e., the amount of crystallized rubber present, depends on two variables, namely, the tension σ and the temperature T . The melting point, T_m , depends on the tension, and the crystallization tension, σ_c , depends on the temperature.

These facts induce one to apply (8) the Clausius-Clapeyron equation for equilibrium between liquid and crystallized rubber depending on temperature and stress. This well-known thermodynamic law relates to the dependence of the melting point upon the tension $dT/d\sigma$, with the difference in length during the extension ΔL and the heat of crystallization r .

One can now test whether the application of this equation gives the same order of magnitude for the heat of melting as was previously measured by L. Hock (13).

For phase transformations of the first order the Clausius-Clapeyron equation has in our case the form

$$\frac{d\sigma}{dT} = -\frac{n}{T} \cdot \frac{1}{\Delta L} \quad (11)$$

When we assume that r is nearly independent of temperature we get by integration

$$\sigma = -\frac{r}{\Delta L} \ln T + \text{const.} \quad (12)$$

For the dependence of the melting point upon the temperature we have to take the quantities that have been determined by Rosbaud and Schmid (23), van Rossem (24), G. von Susich (26) and especially by P. A. Thiessen and Wittstadt (27). If one does that, one obtains for an elongation of 200 per cent and for a temperature of 40°C. the heat of crystallization per gram of rubber to be about 1 cal. This is the same order of magnitude as observed by L. Hock (13).

Therefore it seems reasonable to assume that with increasing tension gradually more and more chains are brought into the extended state and hence can crystallize. If one increases the temperature, the crystallization is hindered by the increased contraction of the chains. When one increases the tension, it is favored. This stands in absolute analogy to a real gas, where temperature increase shifts the equilibrium in the direction of the gaseous state, while an increase in pressure shifts it towards the liquid state.

It may be that in the case of rubber also something like a critical temperature exists, i.e., a temperature above which one cannot obtain interference spots even if one stretches the rubber to its highest degree. Experiments in this direction have demonstrated that it is in fact difficult to obtain interference spots above a certain temperature.

All comparisons of the ideas based on intramolecular statistics with experiment show a perfect qualitative agreement with the observed facts. This might assist in improving the formulas that have been derived to date and in working out some quantitative tests for this new theory of the elasticity of rubber and of rubber-like substances. It is of course evident that the statistical elasticity of rubber only constitutes one side of the total elastic behavior of this material and that its total elasticity is a composed effect, including the action of forces as well as the action of the kinetic movements of the molecules.

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THE STATE OF AGGREGATION OF RUBBER AND OF SUBSTANCES WITH RUBBER-LIKE EXTENSIBILITY

KURT H. MEYER

University of Geneva, Switzerland

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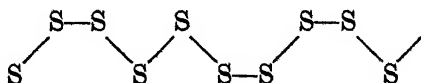
Among the transition states between the classical three states of aggregation it is now possible, on the basis of recent work, to define and understand the characteristics of a certain state,—the state of aggregation of rubber and of other substances with similar mechanical properties.

I. OCCURRENCE OF THE RUBBER-LIKE STATE OF AGGREGATION ("RUBBER-LIKE STATE")

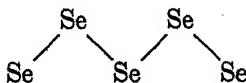
The number of substances that can occur in a rubber-like state is not very large, although considerably greater than is generally realized. The following list shows that this state is not associated with particular elements or chemical groups, and that it is found (A) in polymers of chemically regular or uniform structure, and (B) in irregularly constituted substances with a chain structure.

Class A: Substances in which atoms or atom-groups of the same kind are linked together in chain-like form:—

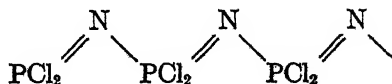
Elastic sulfur (18, 30):



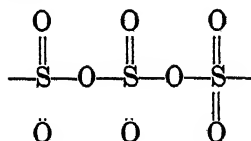
Elastic selenium (23):



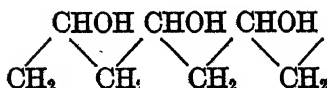
Phosphonitrilic chloride (20, 25, 28):



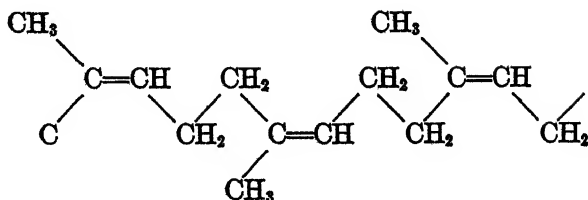
Polymeric sulfur trioxide (3):



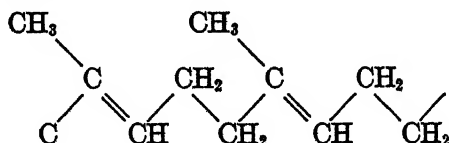
Polyvinyl alcohol (5):



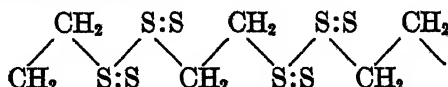
Rubber:



Guttapercha (above 60°C.):



Polyethylene tetrasulfide (24a):



Class B: Chain polymers of irregular constitution:—rubber of medium degree of vulcanization; synthetic rubber, e.g., Buna; polyvinyl acetate (above 60°C.); animal elastic fibers, e.g., in the *Ligamentum nuchae* of the ox; tendinous fibers and elastoidin fibers contracted by heat; muscle fibrils in the uncontracted state.

II. ATOMIC ARRANGEMENT

As x-ray photographs show, no crystalline lattice-like arrangement exists in the rubber-like state in an unstretched object. The x-ray diagram shows only one or more indistinct rings. An interpretation of such "amorphous diagrams," so far as this is possible, has recently been tried by Warren (27) with amorphous rubber. The distribution of intensity is compatible with the assumption that at a distance of 1.5 Å. from each CH₂

group there are two other CH_2 groups and, further, four groups at a distance of between 4 and 5 Å. It must therefore be assumed that the chains do not lie stretched out and side by side, but that, owing to the free rotation around the single bonds, they take up other possible forms.

During the passive stretching of substances belonging to class A the long, primary-valence chains arrange themselves along the fiber direction and "snap" into lattice-like arrangements (9, 12), whereby heat of the nature of heat of crystallization is liberated (6).

The crystalline structures formed during stretching no longer show extensibility; the atoms in these structures are in the same state as in other crystalline bodies. Crystallization thus occurs as a phenomenon accompanying stretching, but has nothing to do with the essential nature of the rubber-like state. This follows also from the behavior of substances in class B. With these the occurrence of crystallization is either entirely absent or incomplete. With vulcanized rubber, for instance, it decreases with increase in the amount of combined sulfur, and hence in the irregularity of the structure, until at about 8 per cent sulfur it disappears entirely, while the characteristic elasticity is not impaired. With polyvinyl acetate there is only one "point" on the equator, according to the observations of Katz (10); this shows that the chains have a parallel orientation but not a lattice-like arrangement.

III. THERMODYNAMIC CONSIDERATION OF RUBBER-LIKE BODIES (1, 8a, 16, 24, 33)

If a stretched rubber-like body is in equilibrium with the deforming tensile force, the equations of thermodynamics can be applied to it. A simplification arises from the fact that the changes in volume during stretching and contraction can be neglected and therefore $A = F$ and $E = H$.

By determining the manner in which the force exerted by a stretched rubber-like body depends on the temperature, it is possible to separate the free energy of contraction A into its components,—the energy component E and the entropy component TS ,—and thereby to arrive at certain conclusions regarding the molecular process occurring during stretching and hence the molecular structure of the rubber-like body itself.

If we denote by K the force exerted and by l the length of the stretched rubber-like body, then we have:

$$K = \left(\frac{\partial E}{\partial l} \right)_T + T \left(\frac{\partial K}{\partial T} \right)_l$$

$$\left(\frac{\partial K}{\partial T} \right)_l = - \left(\frac{\partial S}{\partial l} \right)_T$$

Within a small temperature range K can be expressed as a linear function of T (i.e., the curve can be replaced by its tangent):

$$K = a + bT$$

and thus

$$a = \left(\frac{\partial E}{\partial l}\right)_T \quad \text{and} \quad b = \left(\frac{\partial K}{\partial T}\right)_l = -\left(\frac{\partial S}{\partial l}\right)_T$$

From this the following deductions can be made:

If the force (K) is independent of temperature, then S remains constant during isothermal contraction or stretching; if the force increases with the temperature, S increases during contraction and, if K decreases, S becomes smaller during contraction.

If, within a given range, K varies in proportion to the absolute temperature, i.e., $K = bT$, then $\left(\frac{dE}{dl}\right)_T = 0$; hence an isothermal contraction or stretching is not accompanied by any change in E . If K is smaller than bT , then $\left(\frac{dE}{dl}\right)_T < 0$, which means that E increases during isothermal contraction, while if $K > bT$, i.e., $\left(\frac{dE}{dl}\right)_T > 0$, E decreases during such contraction.

IV. THE MOLECULAR SIGNIFICANCE OF $\left(\frac{dE}{dl}\right)_T$ FOR ELASTIC BODIES

From the standpoint of the mechanical theory of heat, $\left(\frac{\partial E}{\partial l}\right)_T$ denotes the change in the internal potential energy between molecules or parts of molecules during isothermal change of length. If $\left(\frac{\partial E}{\partial l}\right)_T$ is positive, then during contraction forces of attraction are satisfied, either by condensation, crystallization, or formation of exothermic linkages, etc. In the special case of the contraction of an elastically deformed body this can mean that atoms that had been pulled out of the position of least potential energy ("potential trough") by the external force, fall back into this position. The atoms may in such a case have been pulled out of their "potential trough" only by the deformation of the valency angle.

If $\left(\frac{dE}{dl}\right)_T$ equals zero, this means that the work during contraction is to be attributed to the rearrangement of the atoms; it may be said that the thermal motion alone causes contraction.

If $\left(\frac{dE}{dl}\right)_T$ is negative (and therefore $-\frac{dE}{dl}$, i.e., in contraction positive),

this means that the tendency towards rearrangement into a less ordered state is so great that, during isothermal contraction, there is actually more heat absorbed than work given out. The latent heat absorbed is closely akin to heat of fusion: structures in which the atoms are in orderly arrangement become amorphous.

This view is well founded in the case of rubber. The "fusion" can be detected not only thermodynamically but also roentgenographically.

V. THE MOLECULAR SIGNIFICANCE OF $\left(\frac{dS}{dl}\right)_T$ FOR ELASTIC BODIES

As is well known, the entropy is related to the thermodynamic probability, p , which is a measure of the possibilities of rearrangement and states of motion of the molecules, by the equation

$$S = R \cdot \log_e p$$

If, therefore, S increases during stretching and decreases during contraction, this means that during stretching there is a transition from a more ordered to a less ordered state; the range of movements of the atoms becomes greater.

If, on the other hand, S decreases during stretching and increases during contraction, as is the case with rubber at moderate elongations, then during stretching the possibilities of rearrangement and motion of the whole system become more limited; the system becomes more ordered. This process may consist purely in a rearrangement, without change of energy, but may also involve a decrease in internal energy, if crystalline structures are formed with evolution of heat of crystallization.

In figures 1, 2, and 3 the stress-temperature curves for phosphonitrilic chloride (20), vulcanized rubber (16), and an elastic band (17) (*Ligamentum nuchae* of the ox) are shown. It will be seen that, at moderate degrees of extension and at temperatures above 315° Absolute, the stress-temperature curves determined with falling temperatures (upper curves) pass through the origin (i.e., the stress increases in proportion to T). Hence it follows, from what has been said above, that during a change in length no change in energy occurs.

The retractive stress is thus of a fundamentally different kind from the elastic stress in a strained crystal or in strained glass, the atoms of which are pulled, by stretching, out of their "potential trough" into positions of higher energy. *In the rubber-like state, during elastic deformation within large ranges of temperature and elongation, only the molecular arrangement changes, becoming, as a result of stretching, more regular through orientation and therefore thermodynamically less probable. The thermal motion then again restores the unordered state of greatest probability as soon as the external force which produces the deformation allows this.*

This nature of the retractive force, which distinguishes rubber-like bodies from other bodies, we consider to be the best characteristic of the rubber-like state of aggregation.

We see, moreover, that in the case of moderately vulcanized rubber the curves obtained with rising and with falling temperatures coincide, whereas with other types of rubber and with phosphonitrilic chloride the rising-

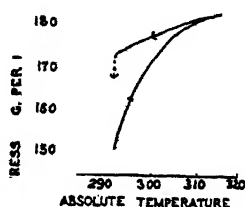


FIG. 1. Stress-temperature curve for polyphosphonitrilic chloride

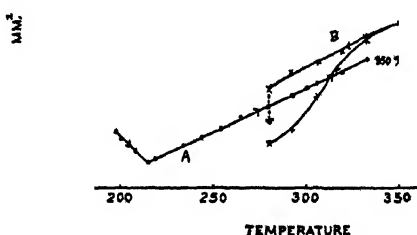


FIG. 2. Stress-temperature curves. A, rubber vulcanized with 8 per cent sulfur; no crystallization. B, lightly vulcanized rubber; gives crystal interferences on stretching.

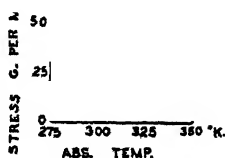


FIG. 3. Retractive stress in an elastic band at 10 per cent elongation in relation to temperature

temperature curve lies below the falling-temperature one. This arises, as can also be shown by x-ray analysis, from the fact that at high temperatures no crystalline phase is present. As the velocity of crystallization of these substances is very low, if the material is rapidly cooled, then the proportionality between stress and absolute temperature characteristic of an amorphous body is obtained. If, now, at constant temperature and

deformation slow crystallization occurs, K decreases; if the material is again heated, heat of fusion is absorbed. Thermodynamically it follows that such a partially crystalline body takes up energy of fusion during isothermal contraction also.

VI. THE STATE OF AGGREGATION OF RUBBER-LIKE BODIES (24)

According to the above, contraction arises from the tendency of the "ordered" system to change into a less "ordered" one. The disorientation is not possible without macroscopic contraction; this forces us to the assumption that atomic groups in the oriented state cannot disorient themselves as do dipoles of a liquid, oriented by an electric field, upon the disappearance of the field. They must consequently be linked together by strong bonds in the direction of stretching. From this it follows that the rubber-like body is built up of "chain molecules." The process of orderly arrangement consists in the stretching out and parallel orientation of these chains.

Thus, even without knowing the chemical constitution, it is possible from the thermoelastic behavior of a rubber-like body to draw conclusions regarding the type of molecule known as "chain molecule."

The stretching out of the chains during elongation, moreover, compels us to assume that in the rubber-like state the atoms or atom-groups in adjacent chains can slip past each other, like the molecules in a viscous liquid. In the other direction they are firmly attached to two adjacent atoms or atom-groups. One may therefore characterize the rubber-like state thus: *that an atom or atom-group is "fixed" in bonds like those that occur in solid bodies and are responsible for their high internal friction ($\eta > 10^{11}$ c.g.s. units) and in the other two dimensions is "fluid," i.e., linked with the remaining neighbors by bonds like those that occur in liquids and are responsible for their viscous properties ($\eta < 10^8$ c.g.s. units).*

In this way the position of the rubber-like state between the liquid and solid states is made clear. We consider it incorrect to speak of two phases, because the conception of a phase requires that a great number of molecules go to make up one liquid or one solid phase. A solid phase may appear alongside the rubber phase only when rubber-like bodies of class A are stretched, but, as already pointed out, it has nothing to do with the rubber-like state. Moreover, there is no ground for the assumption that in purely rubber-like bodies groups of chains, or parts of chains, are bound together into distinct aggregates, termed micelles. Neither can one speak of intermicellar fluid. It would appear incorrect, moreover, to describe rubber-like bodies as anisotropic solids, because the anisotropy is exhibited only in molecular dimensions; macroscopic anisotropy appears only when the body is deformed.

VII. THE INTERNAL FRICTION OF RUBBER-LIKE BODIES. VULCANIZATION

The internal friction during small deformations of small speed has recently been determined by van der Wyk (31) from the damping of torsional oscillations of slightly stretched rubber threads. At the same temperature masticated and vulcanized rubbers show no appreciable difference. Both have a viscosity of the order of magnitude of 10^6 c.g.s. units, so that here the internal processes in the materials cannot be very different; the chain elements slip past one another.

Stretched specimens show a strong anisotropy; perpendicular to the direction of stretching the material is plastically deformable, e.g., a stretched round rubber thread can easily be pressed flat (13), whereas plastic deformation in the direction of stretch, e.g., flowing beyond a certain degree of deformation, encounters a very great frictional resistance, many powers of 10 greater than the former one. Now this second type of friction is very different in the two kinds of material: while masticated rubber continues to flow when subjected to considerable deformations, in the case of vulcanized rubber the frictional resistance is so great that no such plasticity can be observed.

These phenomena can be explained as follows: Whereas in lateral deformation only chain elements slip past one another, in a longitudinal displacement the whole stretched-out chain, i.e., *all* the elements in the chain, must be displaced relative to the adjacent chains. Here, therefore, the frictional resistance is a direct function of the length of the whole chain, which in masticated rubber has a finite value, whereas vulcanized rubber consists of a network of "infinitely long" chains chemically bound together. The bonds are formed by sulfur bridges (21), the nature of which has recently been established as C—S—C linkages (19).

The shorter the chain length, the less is the friction in the direction of stretching and the more quickly does the stretched rubber-like body "relax." In the case of substances with relatively short chains, therefore, the elastic properties can only be observed in deformations of short duration and small magnitude. Substances with still shorter chains form fluids.

On cooling below a temperature that depends on the material, most rubber-like materials change slowly into the amorphous solid state, and some (guttapercha) into the crystalline solid state.

The change from rubber-like state to solid amorphous state does not take place suddenly on cooling, as at a transition point. The rubber-like body at first becomes more viscous, and contraction becomes slower or even practically ceases. The friction between the chain elements, as measured by the damping of oscillations, increases considerably. Below a

certain temperature the body breaks when subjected to considerable mechanical deformation.

The frozen pieces can still be stretched a little, but the atomic or molecular process that takes place during this stretching is now essentially different in nature from that occurring during stretching in the rubber-like state; during stretching in the frozen state the internal energy is increased, the atoms being pulled out of their "potential troughs."

VIII. THE NATURE OF CRYSTALLIZATION BY STRETCHING

As has been pointed out above, during the stretching of substances in class A and of certain substances in class B there are produced structures with lattice-like arrangement, the formation of which can be recognized roentgenographically and thermodynamically. Now many substances consist of a loose network of chains chemically bound together; to this class belongs, for instance, vulcanized rubber, the chains of which are bound into a network by sulfur bridges, so that individual unattached chains ("chemical molecules") practically do not exist, and the whole rubber mass can be considered as one gigantic molecule. In these cases the zones of lattice-like arrangement are smaller in the direction of stretching than corresponds to this chemical "giant molecule"; only parts of the latter are crystallized, other parts being still amorphous. We consider that also in rubber-like bodies containing molecules of finite size, crystallization, at least initially, affects only parts of the chains.

When crystallites appear, it is justifiable to speak of two "phases." The equilibrium between the crystalline and rubber-like phases depends on the temperature and the degree of strain; the greater the strain, the higher is the temperature at which the crystalline phase disappears. This is easily explained by the fact that the strain itself leads to a particular arrangement, different from random orientation, so that the entropy difference, ΔS , between crystalline and non-crystalline phases decreases. If the heat of fusion for rubber is not greatly dependent on temperature, then, according to the equation

$$\Delta E = T\Delta S$$

(where ΔE = heat of fusion and ΔS = change in entropy by fusion) T , the fusion temperature, must rise when ΔS is reduced.

It must further be assumed that with chemically pure substances, i.e., substances constituted by molecules of identical length, provided all chains undergo equal strain there is, corresponding to any given strain, a fusion point. Only at this fusion point do the rubber-like phase and crystal phase coexist. Observations on this point are lacking, and, moreover, would be difficult on account of the slowness of crystal formation, as has

recently been pointed out by Thiessen (29). With impure rubber-like bodies such as vulcanized rubber, on the other hand, a fusion range is to be expected.

A process analogous to the "fusion" of stretched and crystallized rubber, fibrous sulfur, etc. (14) is the contraction of tendinous fibers and elastoidin fibers on heating, whereby they change over to the rubber-like state (Rolle's phenomenon). Here also the fusion point is raised by strain, an effect which has been exhaustively studied by Wöhlisch (32) and recently by Fauré-Fremiet (2).

IX. THE LINKAGE POINTS

In the crystalline structures formed by stretching, the chain elements are held or linked together by the lattice forces, so that slippage no longer occurs. At these points of linkage the chains will therefore behave as though they were firmly joined or "knitted" together. As a result the plasticity of the rubber-like body will be reduced. If these linkages are destroyed, a change which may be brought about by raising the temperature, the retractive force in the oriented chains suffices to overcome the friction of the whole chain; the rubber relaxes and the elastic deformation changes to a permanent plastic deformation. As is well known, this is made use of in the rubber industry when crude rubber is milled above its highest fusion temperature and pressed in molds. By adding solvents, also, the fusion point can be lowered and hence the plasticity increased. Conversely, at low temperatures there occurs a phenomenon that recalls vulcanization, and may be described as vulcanization by cold; the crystalline linkage points are increased in number by the cooling.

As already stated above, there are present in vulcanized rubber sulfur bridges which bind the chains together. These permanent chemical bonds are not sensitive to temperature and also cannot be broken by solvents; they prevent, as is readily understandable, plastic deformation even at elevated temperatures. Precisely analogous phenomena are shown by other polymers when their chains are bound together into a network, as, for instance, in the case of collagen fibers by formaldehyde (16).

Now when rubber is vulcanized with a small amount of sulfur, this does not suffice to bind all the chains into a network. Instead, there is produced a rubber-like body in which a number of unattached chains are embedded in a network of chains chemically bound together. An "unvulcanized" system and a "vulcanized" system are thus intermingled. Such mixed systems have been studied, with reference to their elastic and viscous properties, by Ferri (17). On stretching, both systems are at first subjected to stress; the unvulcanized chains, however, are then able to slip past each other, disorient themselves, and relax, while the net-like system remains

in the stressed condition. If the rubber is stretched further, these phenomena reappear; the stress increases and then falls off again owing to relaxation. On removing the external tensile force the vulcanized system contracts and thereby compresses the relaxed unvulcanized system, so that an equilibrium is set up between the contracting network and the compressed free chains. These free chains can relieve themselves of the compression by gradual relaxation, so that the body continues to contract very slowly, or "creep back," until the original state is regained.

If such a rubber is allowed to remain under the influence of a constant stress, e.g., a weight, its length continues to increase for a considerable time, that is, it "flows." Finally, however, when its net system is fully extended, the increase in length ceases, whereas an unvulcanized amorphous rubber would continue to flow or else would break.

Mixed systems of interlinked chains (networks) and free chains appear to us interesting, because during passive extension they show the same behavior as smooth muscles of the lower animals. The plastic and elastic properties of these have recently been fully described by Jordan (7). After what has been said above it is not necessary to point out that we do not share Jordan's views regarding the process of relaxation, in which he considers that an intermicellar liquid and micelles play a part. We believe rather that muscles are to be regarded as a system of interlinked and free protein chains.

X. SWELLING AGENTS

If a rubber-like body is subjected to the action of liquid substances which exert on the atoms of the chain elements a force of attraction equal to or greater than that between the atoms themselves, the molecules of the liquid penetrate between the chains; the volume of the rubber-like body increases, that is, it "swells." If the chains have a finite length, they gradually become entirely surrounded by the solvent, and the swollen mass is transformed into a solution. If they are joined together by bridge-like bonds the swelling is limited; penetration of the liquid is possible only up to a certain volume increase, that is, up to the point where the network is fully extended.

Swelling agents lower the fusion point of crystalline chain polymers and the softening point of amorphous ones. By means of suitable swelling agents it is possible almost as a general rule to convert solid substances consisting of chain polymers into the rubber-like state. As examples we may quote the action of glycerol on dry gelatin, by which the elastic hectograph compositions are produced, the action of formic acid on silk (22), and of formamide on tendinous fibers. In the elastic fibrils of living organisms a certain water content is necessary to produce the rubber-like properties.

XI. CONSIDERATION OF THE FORM AND MOVEMENTS OF THE CHAINS IN THE RUBBER-LIKE STATE

As has been stated above, it follows from the elastic properties that the chains are flexible and can assume various forms. In spite of the bonds in the chain the chain elements are movable relative to one another. This conclusion is supported by the following fact: Both polyphosphonitrilic chloride and polymeric sulfur are formed, with absorption of heat, from the lower-molecular ring compounds $(\text{PNCl}_2)_2$ and S_8 . The entropy content of the polymerized substances is therefore greater than of the rings. From this it follows that atoms or atom groups have more possibilities of rearrangement than in the rings; the chain elements are more mobile than in the rings (15).

Estimations of the form of the whole chain in the isotropic rubber-like state have been undertaken by Guth and Mark (4) and by Kuhn (11). The latter considers that the most probable form is a very loose ellipsoidal skein, which is, so to speak, "dissolved" within a mass formed by the neighboring chains. "The chains thus interpenetrate one another in a complicated manner."

The statistical calculations undertaken by Guth and Mark and by Kuhn showed that in the unoriented state the distance between the two ends of a chain consisting of n members each of length z lies between $z \cdot n^{\frac{1}{2}}$ and $z \cdot n^{\frac{1}{2}}$, whereas the chain when stretched out has a length of $z \cdot n$.

XII. CONCLUSION

A theoretical inquiry into the state of aggregation of rubber-like bodies seems to us to be of interest, not only in relation to the technical importance of rubber, but even more because of its close relation to biological questions. Properties characteristic of the rubber-like body are found in many animal tissues; reference may be made, for instance, to the elastic fibers, to the astonishingly high elastic extensibility of red blood corpuscles, which according to Seifriz (26) can be reversibly extended to many times their original size by means of the micromanipulator, and to the extensibility of the protoplasm of amoebae, observed by Seifriz. These systems, like all living systems, are subject to the same physical and chemical laws as non-living substances. In general it is easier to study the laws governing the non-living, more amenable materials. There is therefore ample justification for the task of first studying the laws governing chemically defined rubber-like bodies, in order subsequently to be able to apply these laws to biological problems.

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THE DISSOCIATION CONSTANTS OF MONOCARBOXYLIC ACIDS; THEIR MEASUREMENT AND THEIR SIGNIFICANCE IN THEORETICAL ORGANIC CHEMISTRY

JOHN FREDERICK JAMES DIPPY

City of Cardiff Technical College, Cardiff, Great Britain

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I. INTRODUCTION

Measurements of the dissociation constants of monocarboxylic acids in aqueous solution have contributed very materially to our knowledge of the polar effects of substituent atoms and groups in organic molecules. For the most part the organic chemist is concerned with qualitative considerations, and hence usually takes into account only the relative strengths of acids. Nevertheless, it is imperative that dissociation constant data

should be the outcome of work providing a high degree of accuracy, and therefore the old less-reliable data must be superseded by the modern values whenever these are available. The experimental technique and methods of computation have undergone rapid development in recent years, and, as a consequence, dissociation constants of organic acids in aqueous solution can now be determined with considerable accuracy.

The writer has for the last eight years been engaged in the measurement of the strengths of monobasic organic acids in water at 25°C. by a semi-precision conductivity method, and the work has now reached a stage at which a review of the whole will be advantageous. The entire series of dissociation constants are discussed in relation to each other and in the light of recent contributions to the subject of the polarity of groups.

A brief account is given of those aspects of the conductivity method with which the organic chemist may be unfamiliar, and, in addition, arguments are advanced in favor of the use, in organic discussions, of dissociation constant data relating to aqueous solutions and a fixed temperature.

II. MEASUREMENT OF ACID STRENGTHS

A. Early attempts at comparison

It is interesting to trace the early efforts directed at the determination of the acid strengths or "avidities," as they were then abstractly designated. Julius Thomsen, in 1854, attempted to compare, by a thermochemical method, the avidities of two acids competing for a limited quantity of base in aqueous solution, and some twenty years later the investigation was extended by Wilhelm Ostwald, who resorted to a variety of procedures in an attempt to ascertain more accurately the competing avidities. Perhaps the best known of these methods is that of comparing the effects of various acids on the hydrolysis rates of well-known organic compounds, such as methyl acetate and acetamide (this investigation has also the distinction of having marked the beginning of the systematic study of homogeneous catalysis).

In seeking a different method of procedure Ostwald turned his attention to the possibilities of the electrical conductivity of acid solutions (138), and the first experiments concerned hydrochloric, acetic, dichloroacetic, and certain other acids. Kohlrausch had already established the experimental procedure, and by means of it discovered two fundamental laws governing the conductance of salts in aqueous solution (*viz.*, the square-root law and the law of the independent migration of ions). It should be noted that these earlier results were expressed as molecular conductivities (μ), defined as the product of the specific conductance and the number of cubic centimeters containing 1 gram-molecule of the solute, although,

later, molecular conductivity was replaced by equivalent conductivity (Λ), which relates to 1 gram-equivalent of the solute. Moreover, the Siemens unit was then the unit of resistance, and hence the values of Λ in the older literature appear lower than those deduced on the present basis of the ohm; these conductivity data may be converted to the present standard by multiplying by the factor 1.066.

The electrical conductivity method proved of great use to Ostwald, for he succeeded in obtaining molecular conductivities at fixed concentrations which presented a relative order completely in harmony with the sequence of avidities arrived at by other methods of comparison; furthermore, a satisfactory explanation of these conductivity results was soon forthcoming.

A year prior to this Arrhenius (2) had published his far-reaching theory of the ionic dissociation of electrolytes. This hypothesis, which accounted so strikingly for the abnormalities in Raoult's cryoscopic measurements, soon led to a means of representing the strength of an acid, and in consequence of its application in this connection the concept became greatly enhanced in value.

It was pointed out by the antagonists of the ionic hypothesis that in the case of strong electrolytes the mass action law did not appear to govern the equilibrium which was supposed to exist between molecules and ions. To counter this, Arrhenius suggested that a better test of the theory would be provided by electrolytes in which dissociation varies over a wider range upon dilution. Experimental data for this class of electrolyte were furnished by Ostwald, who in a short space of time examined about two hundred and forty organic acids in aqueous solution (140). The results proved that the law of mass action was obeyed reasonably well here, and, furthermore, led to the familiar dilution law expression which serves to connect K (dissociation or ionization constant), α (degree of dissociation), and c (molecular concentration). The equation is

$$K = \frac{\Lambda_c^2 \cdot c}{\Lambda_0 (\Lambda_0 - \Lambda_c)}$$

where Λ_c and Λ_0 are the equivalent conductivities at concentration c and at infinite dilution, respectively. It was found to hold good for further weak acids (18, 164), for phenols (5), and for amines (25), and since that time, i.e., for the past forty years, an ever-increasing body of evidence of this kind has been accumulating.

B. Thermodynamic dissociation constants

Until recent years the Ostwald constant had been accepted as a quite satisfactory means of expressing acid strength. For weak acids, although

strictly incorrect, it is certainly an approximation, and is now referred to as the classical dissociation constant ($K_{cl.}$). With the elucidation of the anomaly of strong electrolytes, the problem of weak electrolytes has also undergone further scrutiny, and it has become evident that the Ostwald method of computing acid strengths has its shortcomings.

Firstly, it was wrongly assumed that ion mobility is independent of concentration; the Arrhenius degree of ionization, $\alpha = \Delta_c/\Delta_0$, must be replaced by Δ_c/Δ_∞ where Δ_∞ , although referring to complete dissociation, ascribes to the ions the mobilities obtaining at concentration c . The means of deducing Δ_∞ from the experimentally determined Δ_0 is provided by Onsager (136), who has modified the Debye-Hückel treatment. Banks (11) has produced a simplified form of the Onsager expression which renders the process of calculation less laborious, *viz.*,

$$\Delta_\infty = \sqrt{\Delta_0^2 - 2b(\Delta_0 \Delta_c c)^{1/2}}$$

where b is the Onsager slope, which, for an aqueous solution at 25°C., is $(0.2271\Delta_0 + 59.78)$.

Secondly, in the mass action equation activities must take the place of stoichiometric concentrations, *i.e.*,

$$K = \frac{a_H \cdot a_X}{a_{HX}}$$

Since a , the activity, is given by $c \times f$ (where f is the activity coefficient), the equilibrium constant becomes

$$K = \frac{c_i f \times c_j f}{c_u}$$

where $c_i (= c\alpha)$ and $c_u (= c(1 - \alpha))$ represent the concentrations of ionic and undissociated species, respectively. By taking logarithms and substituting the Debye-Hückel expression, $-\log f = A\sqrt{c_i}$, the above equation becomes

$$\log K = \log \frac{c_i}{c_u} - 2A\sqrt{c_i}$$

where $2A$ is a constant which has been evaluated as 1.01 (for details see reference 35). All dependable dissociation constants are calculated on this basis and are called "true" or "thermodynamic" constants ($K_{th.}$).¹ The vast majority of organic acids studied so far possess strengths ranging from 10^{-5} to 10^{-3} , and here the values of $K_{th.}$ are invariably less than those of $K_{cl.}$.

¹ The terms $K_{th.}$ and $K_{cl.}$ are further contractions of the terms $K_{therm.}$ and $K_{class.}$ employed in previous papers.

Examination of results for a given acid will show, where the accuracy is great enough, that $K_{cl.}$ falls as dilution increases, in contrast to $K_{th.}$ which remains constant, until finally, at high dilution, the former approaches the value of the latter, as is to be anticipated on theoretical grounds. This feature is illustrated by the data (for aqueous solutions at 25°C.) shown in table 1.

In the case of acids the dissociation constants of which do not fall below 10^{-5} no allowance is made for the conductance of the water used in making the solutions, since these acids are, relatively, so very much stronger than carbonic acid as to depress almost completely the ionization of the latter. For investigations of ordinary organic acids, therefore, the

TABLE 1
Variation in $K_{cl.}$ and $K_{th.}$ with dilution

| ACETIC ACID (126) | | | DL-MANDELIC ACID (12) | | |
|-------------------|---------------------------|---------------------------|-----------------------|---------------------------|---------------------------|
| 10°C | 10 ⁴ $K_{cl.}$ | 10 ⁴ $K_{th.}$ | 10°C | 10 ⁴ $K_{cl.}$ | 10 ⁴ $K_{th.}$ |
| 5.91153 | 1.801 | 1.748 | 6.2307 | 4.094 | 3.877 |
| 3.44065 | 1.792 | 1.749 | 4.1414 | 4.060 | 3.874 |
| 2.41400 | 1.788 | 1.750 | 2.9045 | 4.047 | 3.880 |
| 1.36340 | 1.785 | 1.752 | 2.2938 | 4.027 | 3.866 |
| 1.02831 | 1.779 | 1.750 | 2.1454 | 4.030 | 3.883 |
| 0.21844 | 1.770 | 1.750 | 1.4006 | 3.996 | 3.873 |
| 0.15321 | 1.766 | 1.750 | 1.3190 | 3.987 | 3.863 |
| 0.11135 | 1.768 | 1.753 | 0.73771 | 3.936 | 3.850 |
| 0.028014 | 1.759 | 1.752 | 0.22647 | 3.869 | 3.866 |

specific conductance of the conductivity water is measured simply to ensure that the specimen is acceptable.

C. Limiting equivalent conductivities and ion mobilities

In order to determine Λ_0 , separate experiments must be made on solutions of a soluble salt of the monobasic acid. The sodium salt is invariably employed for this purpose, since it is a strong electrolyte (uni-univalent) and yields results which may be extrapolated to zero concentration in the plot of Λ_c against \sqrt{c} . Actually, in the extrapolation process Kohlrausch's square-root equation is superseded by Onsager's equation, meaning that the plot of Λ_c/\sqrt{c} should not only be linear, but the slope should approach the theoretical value ((0.2271 Λ_0 + 59.78) given by Onsager for aqueous solutions at 25°C., i.e., the conditions applying to most conductivity measurements).

In the case of a salt derived from a strong acid and strong base solvolysis is negligible, and good agreement with Onsager's equation is reached,

provided the simple "normal" solvent correction is applied to the measurements, i.e., for aqueous solutions, allowance having been made for the conductivity of the water, which consists in subtracting the specific conductance of the water from that of the given solution. The sodium salts of most organic acids, however, are appreciably hydrolyzed in solution, and here the "normal" solvent correction proves to be excessive. In arriving at the true correction the hydrolysis must also be taken into account, and a means of calculating the combined solvent and hydrolysis correction has been proposed by Ives (97) and by Davies (34). Lately, however, Banks and Davies (12) have succeeded in showing, by a series

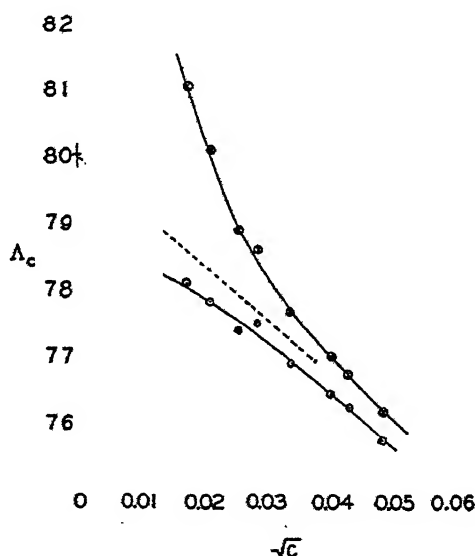


FIG. 1. Plot of Δ_c against \sqrt{c} for sodium *p*-toluate. \otimes , uncorrected; \odot , "normal solvent" corrected. $\Delta_0 = 80.0$. The dashed line is the Onsager slope.

of precision measurements on sodium mandelate in samples of water differing in quality, that it is incorrect to assume that carbonic acid is the only impurity in ordinary conductivity water; this assumption is implicit in the suggested method of correction and apparently leads to slight over-correction. If it is agreed, therefore, that there exist traces of various other impurities in the average specimen of conductivity water, it seems that no exact method of correction can be applied to the results from hydrolyzed salts. It is proposed by Banks and Davies that a value of Δ_0 can be obtained in these cases by suitably inserting a line possessing the theoretical Onsager slope. This method resembles the expeditious procedure employed by the present author (as the result of an earlier suggestion

by Dr. C. W. Davies), in which values of uncorrected and "normal" corrected Λ_c are both plotted against \sqrt{c} , and, where the curves begin to diverge seriously, a straight line is drawn representing the Onsager slope 50, 51) (for all the organic salts studied this line is inclined at an almost constant angle). Figure 1, representing the results for sodium *p*-toluate (due to the author), is typical; it will be seen that the Onsager slope approaches more closely the "normal" solvent-corrected points, agreeing with the observations of Banks and Davies on sodium mandelate. This method provides an accuracy sufficient for the purpose in hand. A divergence of 0.2 unit in Λ_0 affects the dissociation constant of benzoic acid by less than 0.1 per cent, which is negligible, since the constant is expressed, for ordinary purposes, to three significant figures only. Values of Λ_0 obtained in this way have proved reasonably reproducible, and the good agreement with results of other investigators on the sodium salts of acetic, benzoic, and *m*- and *p*-chlorobenzoic acids has given justification for the method (53).

Although most workers apply the square-root relation to their results for aqueous solutions, there exists an alternative method of extrapolation which has also been adopted in modern investigations. This is due to Ferguson and Vogel (59), who employ the formula

$$\Lambda_c = \Lambda_0 - Bc^n$$

where B and n are arbitrary constants estimated by a graphical method for each electrolyte.

In arriving at the value of Λ_0 (acid) from Λ_0 (salt) on the basis of the law of the independent mobility of ions, the data for the limiting mobilities of the hydrogen and sodium ions are used. Computation of actual mobilities involves a knowledge of transport or transference numbers, since the mobility of a specified ion (l) is the product of the equivalent conductivity of an electrolyte containing the ion and the transport number of the ion relating to that electrolyte at the given concentration. Recent and very reliable determinations of transport number by the moving-boundary method (121), coupled with precision measurements of conductivity on aqueous solutions of hydrogen chloride and sodium chloride (154), have led to values of 50.10 and 349.72 for the limiting mobilities of sodium and hydrogen ions, respectively, in water at 25°C. (127). Of course, on the other hand, Λ_0 (salt) can be converted to Λ_0 (acid) simply with a knowledge of $l_{\text{H}} - l_{\text{Na}}$, which may be obtained from independent measurements of the limiting equivalent conductivities of suitable electrolytes (e.g., $\Delta_0_{\text{HCl}} - \Delta_0_{\text{NaCl}}$); however, these additional determinations are not necessary now that accurate ion-mobility data are available.

Jeffery and Vogel (101) have published alternative values for the

mobilities of the sodium and hydrogen ions, derived from their own conductivity measurements, to which they apply the Ferguson-Vogel formula. It has been pointed out that the use of these mobilities leads to values of Λ_0 (acid) which are 1.4 units (mhos) smaller than those based on the MacInnes-Shedlovsky mobilities, and consequently the values of K are not strictly comparable (40); the latter mobility data appear to be finding the more general acceptance. Until the new data were forthcoming, those of Noyes and Falk (135) and of Kendall (108) were employed.

The mobilities of anions (l_a) derived from various monobasic organic acids vary considerably in magnitude, and some interesting generalizations can be traced upon examination of the data recorded by the present author and his coworkers for some ninety different anions.

In the vast majority of cases the ion mobilities range between 27 and 33 units, and as a rule it can be said that, as the weight and size of the ion increase, the mobility is diminished, and there appears to be no definite limit, which is contrary to the belief held by Ostwald (139) that l_a is not altered further when the ion contains as many as twelve atoms. Nevertheless, it is true that the smaller the ion the greater is the effect of bringing about a given increase in size; this is best illustrated by the following values of l_a for saturated and unsaturated aliphatic acids: acetic, 40.9; *n*-butyric, 35.1; *n*-valeric, 33.4; *n*-hexoic, 30.8; *n*-heptoic, 29.2; *n*-valeric, 28.8; *n*-nonoic, 27.1; *cf.* acrylic, 37.4; vinylacetic, 34.8; allylacetic, 33.0. It has also been noted that in the case of aliphatic monocarboxylic acids, chain branching reduces the speed of migration of the ion, so that for l_a in isomeric ions the order of magnitude is primary > secondary > tertiary, e.g., the anions of *n*-valeric, isovaleric, and trimethylacetic acids possess mobilities of 33.4, 32.7, and 31.9, respectively. A similar conclusion can be drawn from the values of l_a in the cases of *n*-butyric and isobutyric (35.1 and 34.1) and hexoic and diethylacetic (30.8 and 30.4) acids.

In the benzoic and phenylacetic series, the mobilities of the halogen-substituted ions are arranged, for greater part, in the order $I < Br < Cl < F$ (the converse of the order of the halide ions). The effect of a bulky substituent may be distinguished in the *o*-phenyl- and *o*-phenoxy-benzoic ions, which possess mobilities of 23.5 and 23.3, respectively, compared with 33.4 for the benzoic anion. It has been made very clear, however, that bulk and weight are not the only factors influencing the movement of the ion, for it seems that the values of l_a for methyl- and methoxyl-substituted ions are, on the whole, smaller than might be expected when comparison is made with those for halogen- and nitro-substituted anions. Furthermore, examination of the four series (benzoic, phenylacetic, β -phenylpropionic, and cinnamic) shows that the effects of substituting a group in the *o*-, *m*-, and *p*-positions are not identical, although there appears to be no rule as

to the change brought about by moving the substituent from one position to another. The mobilities of the anions of *cis*- and *trans*-cinnamic acids are distinctly different (32.6 and 30.4, respectively); the *cis*-form is more compact and possibly is hindered less in its movement. In the aliphatic systems, also, it has been shown that isomeric ions do not possess identical mobilities (99, 41).

D. The conductimetric method of measurement

Although the procedure is still, in principle, that developed by Kohlrausch, vast improvements in equipment and technique have been made since his time.

The induction coil as a source of current is now replaced either by a Vreeland generator (first recommended by Taylor and Acree (160)), or, more commonly, by a thermionic valve oscillator (introduced by Hall and Adams (74)), which produces a constant high-frequency alternating current sensibly free from unidirectional component. Several types of conductivity cell have been introduced from time to time for various purposes; probably the best known are the pipet cells devised by Washburn (165) and the cell of the dipping-electrode type due to Hartley and Barrett (88). Cells of the bottle type have also been used to advantage by numerous workers (100, 50). Silica or borosilicate glass (usually Pyrex or Jena 16 III grade) is used in the construction of the cells, and the electrodes are almost invariably of platinum, greyed or blacked according to requirements. A standard solution of strong electrolyte, conventionally potassium chloride, is employed for calibration of the cell. The first data for such a solution were supplied by Kohlrausch and Holborn (112, 113), although since that time fresh determinations have been made, effecting very small changes, the most recent being due to Jones and Prendergast (107); for cells possessing a relatively low cell constant, the "intermediate cell" method (35) is recommended. In order that reasonable resistances may be measured (the desirable range is 1000 to 50,000 ohms), a variety of cells should be available to cope with solutions covering a wide range of concentration; consequently, judgment must be exercised in the selection of a cell for any given measurement.

Two types of bridge wire are now in general use. There is the straight wire, which is similar to that employed originally by Kohlrausch and by Ostwald, except that the effective length is greatly extended by the attachment of selected resistances at either end of the wire. The second type, namely, the drum-wound form, is compact but is said to have its disadvantages (35). All the standard resistances of the bridge assembly are of the low-inductance quality. It is essential that outside disturbances be eliminated if satisfactory results are to be obtained; thus the current

generator must be enclosed by an earthed metal screen. During measurements the balance-point may be obscured somewhat (especially where resistances are high) by capacitance effects arising from the cell, but this difficulty is largely overcome by use of a suitable variable condenser in parallel with the standard resistance. The whole problem of bridge assembly and procedure has been dealt with in detail by Jones and Josephs (106) and by Shedlovsky (154), who suggest numerous refinements.

A telephone of low resistance, tuned to the frequency of the generated current (approximately 1000 cycles per second), is used as detector, sometimes in conjunction with a valve-amplifier, although a loud-speaker device is preferable where difficulty is encountered with the audibility of the note. The greater advantages of a visible indication of balance-point are obvious, and an apparently satisfactory device has now been provided, *viz.*, the null-point indicator ("electric eye"), which embodies a small cathode-ray tube; it is claimed to be extremely sensitive, and doubtless will receive wide application in course of time.

The most satisfactory conductivity water for general use is that described by Kendall (109) and referred to as "equilibrium water." Its chief impurity is carbon dioxide present in such a concentration as to be in equilibrium with atmospheric carbon dioxide; the specific conductivity of this water is 0.8–0.9 gemmho. Various stills have been devised for the preparation of "equilibrium water," although others have been described which are capable of supplying water of even a higher grade. For most conductivity investigations a range of solutions of varying concentration is required; at the present time they are made up by the weight-dilution procedure (proposed by Whetham (171)), as the old method of successive volume-dilution imposed limitations which often led to serious errors. In determining the conductivity of a series of solutions covering a range of concentrations, it is better to make the initial measurement on the strongest solution and to continue through the run with increasing dilution; the adverse effect of adsorption of solute at the electrodes is thus minimized.

The dissociation constants of organic acids recorded in the older literature are less accurate, not only on account of lack of refinements in the procedure but because the purity of the compounds was so frequently open to doubt. This is well illustrated in the fatty acid series, where it has been found that the closest agreement with recent semi-precision measurements (41) is to be found in the determinations of the only investigator (63) who stated consistently the purity of his materials.

It is essential also that precautions should be taken to safeguard the purity of the salts employed in the determinations. These are made from pure acids by titration with sodium hydroxide (carbonate-free), and the

solid product is isolated by evaporation and purified by crystallization from alcohol. Successful measurements have been made, however, on the aqueous solutions made directly by titration; in many cases there is no alternative but to proceed in this way, e.g., with nitro-substituted acids and unsaturated aliphatic acids (40).

E. Other methods of measurement

Apart from the conductimetric method there are two other reliable procedures now employed in obtaining the dissociation constants of acids, *viz.*, the potentiometric titration method and the alternative E.M.F. method of Harned. In the former procedure, solutions of the acid are partially neutralized with known quantities of base and the pH of the solutions is determined by means of a suitable electrode made up into a cell with a reference electrode, usually the calomel half-cell. Various electrodes may be used with the solution under investigation; these include the ordinary hydrogen electrode, the glass electrode, and the quinhydrone electrode. Special precautions have to be observed in operating each of these. The following is the choice of electrodes made in the more important investigations of dissociation constant: Branch, Yabroff, and collaborators (178, 23, 24, 19, 179) on substituted phenylboric and the hydroxybenzoic acids (hydrogen electrode); Bennett, Brooks, and Glasstone (14) on substituted phenols (glass electrode); Kuhn and Wassermann (114) on halogeno- and hydroxy-benzoic acids (quinhydrone electrode). It should be realized that the potentiometric method has its shortcomings: briefly, there is doubt regarding the actual potential of the calomel electrode on the hydrogen scale, and, again, uncertainty is introduced by the employment of a liquid junction. Moreover, the experimental accuracy achieved with solutions of sparingly soluble acids compares unfavorably with that obtained in conductimetric measurements.

The alternative cell method has been exploited very successfully by Harned and coworkers (83, 84, 86). In measurements upon four aliphatic acids at temperatures ranging in 5° intervals from 0° to 60°C., they have employed a cell without liquid junction. This consists of a Ag-AgCl electrode and the hydrogen electrode in a solution of the fatty acid and its sodium salt and sodium chloride. From the E.M.F. determined for different concentrations of acid and salt, the thermodynamic dissociation constant is calculated (a concise account of the method of calculation has been given by Glasstone (65)). A high degree of accuracy has been achieved by Harned, and later workers have also used the method to advantage in determining dissociation constants of further acids at a variety of temperatures (see page 162).

F. A survey of the available modern data

All of the dissociation constant data for monobasic organic acids (also for phenols and bases) that have been derived by the modern, more reliable methods are assembled in the appendix to this paper.

Vast numbers of classical constants were published by earlier workers, notably by Ostwald, and they may be used as confirmatory evidence in discussion, especially when a number of them are recorded by a single investigator; nevertheless, no importance must be attached to relatively small differences in such constants. When results are expressed in terms of $K_{cl.}$, there exists the factor introduced by considerations of the concentrations of the acid solutions; it has already been seen that $K_{cl.}$ is not independent of concentration (page 179). If two acids differ widely in solubility, the conductivity measurements might involve solutions differing vastly in dilution, and thus a comparison of the classical constants is rendered invalid. This objection is particularly significant in the fatty acid series.

III. THE EFFECT OF TEMPERATURE AND SOLVENT VARIATION*A. Temperature dependence*

Broadly speaking, it can be said that at ordinary temperatures the conductivity of an aqueous solution increases by about 2 per cent per degree rise, although it is possible for temperature elevation to bring about a fall in specific conductivity. With weak electrolytes the temperature coefficient is determined by two factors: namely, the mobilities of the ions, which invariably increase with rising temperature, and the degree of dissociation, which reaches a maximum. At temperatures above this maximum the increase of mobility may not be great enough to offset the effect of decreased dissociation, and with such a state of affairs the measured conductivity may diminish upon elevation of temperature. It is not surprising, therefore, to find that the ionization constants of organic acids have been observed to pass through a maximum (K_m) as the temperature increases. A number of earlier workers, including H. C. Jones, A. A. Noyes, and Schaller, made measurements on organic acids at several temperatures ranging from 5° to 100°C., and although the temperature (θ) of maximum dissociation constant (K_m) was not determined in any case, it was clear that the dissociation constant did not necessarily increase with rise of temperature. In recent years thermodynamic dissociation constants have been recorded for a limited number of acids (formic (84), acetic, propionic (83), *n*-butyric (86), chloroacetic (175), glycolic (134), lactic (128)) at a variety of temperatures, and Harned and Embree (84) show by means of such data that when $\log K_t - \log K_m$ is plotted against

$t - \theta$ (where t is the temperature relating to the dissociation constant K_t), a curve is obtained which approaches parabolic form in the region extending 75°C. on either side of θ , so that for ordinary purposes the following empirical equation satisfactorily connects temperature and the maximum ionization constant,

$$\log K_t - \log K_m = -p(t - \theta)^2$$

where p is a general constant, 5.0×10^{-5} degree⁻². Actually, the values of θ and K_m are obtained by plotting $\log K + pt^2$ against t ; the slope of the resulting straight line gives $2p\theta$, and the intercept at $t = 0^\circ\text{C.}$ is $\log K_m - p\theta^2$. This relationship must already be regarded as of great significance.

As a generalization, it may be said that the stronger the electrolyte the lower the temperature of K_m , and it is possible, theoretically, that values of K_t may range themselves in different relative orders according to the temperature. Thus, Harned and Embree have advocated that in a comparison of acid strengths in relation to constitution, it is better to select data for K_m , because then $\Delta H = 0$ in every case, and consequently complications arising from possible differences in heat capacity and entropy effects are eliminated.

Subsequently, both Hammett (78) and Baker (7) also suggested that such complications might affect the relative order of the dissociation constants of acids. The significance of this objection has been considered by the present author (39), who points out that the facts actually indicate, however, that safe conclusions *can* be reached from K_{tA} data relating to a fixed temperature. With evidence of this kind consistent and satisfactory results have been obtained in past discussions, and, moreover, quantitative relationships have been satisfied (see section V); this can scarcely be described as fortuitous. Indeed, it might be anticipated that the differences which are liable to cause complications will be negligible in a series of similar acids (i.e., acids possessing like strengths). The theoretical objection can be tested by taking into account Harned's multi-temperature data for acetic, propionic, and *n*-butyric acids (83, 86). It is seen below that the order is indisputable, no matter whether the values of K relate to a fixed temperature or to θ .

| ACID | K_{10° | K_{25° | K_m |
|------------------------|----------------|----------------|-------|
| Acetic..... | 1.729 | 1.754 | 1.76 |
| Propionic..... | 1.326 | 1.336 | 1.34 |
| <i>n</i> -Butyric..... | 1.576 | 1.515 | 1.57 |

It is also noteworthy that Pitzer's alternative formula (144), relating K and t , involves the assumption that the entropy change and the change

in heat capacity for monobasic acids are constant, and this is given justification by the experimental facts.

It may be concluded, therefore, that evidence goes far to show that accurate values of K_{a} for acids at 25°C. yield an order of acid strengths acceptable for purposes of discussion, despite the matter of temperature dependence.

B. The effect of changing the solvent

Exceedingly few measurements have been made on solutions of organic acids in non-aqueous solvents, although those which are available make it clear that dissociation in these solvents is substantially less than in water, as might be expected with media of lower dielectric constant. The difficulties encountered in purifying and handling organic solvents are far greater and, moreover, the resistances to be measured are of a higher order. Again, in the case of aqueous solutions of acids, the effect of change in the quality of the solvent upon the conductivity is inappreciable (actually, since carbonic acid is the chief impurity in conductivity water it is unnecessary, in the case of most organic acids, to correct for the solvent conductivity), but with acids in non-aqueous solution the quality of the solvent is a much more important factor (the influence of traces of water is appreciable), and no reasonably reliable method of correction exists; consequently, a grave difficulty is encountered here in interpreting the results. Thus it appears somewhat invidious to attempt to compare the scanty and less trustworthy dissociation constant data for non-aqueous solutions of weak acids with those relating to water.

The bulk of the available data refer to solutions in methyl and ethyl alcohols, and the most extensive conductivity measurements are those of Goldschmidt and collaborators (66) and of Hunt and Briscoe (94). The last-named authors also examined a small number of acids in acetone but did not record any dissociation constants. By using an arbitrary method of correction for the conductivity of the solvent, Goldschmidt obtained constant values of K for alcoholic solutions, but Hunt and Briscoe, by simply deducting the conductivity of the solvent from the measured conductivity, arrived at very irregular values of K . These investigations, together with unpublished work by the present writer on the conductivity of benzoic, phenylpropionic, cinnamic, and other acids in acetone, serve to show that, before wholly satisfactory dissociation constants can be deduced by this method, the problem of true solvent correction needs thorough investigation.

A small number of approximate dissociation constants for organic acids (and bases) in non-aqueous solution have been determined potentiometrically (73, 67, 174, 26, 130a); although it is not certain how reliable

these constants may be, they seem to be comparable with the conductimetric data.

Wynne-Jones (176), after a consideration of certain of these results, suggested that organic acids of similar type do not give the same order of strengths in all solvents, and, to exemplify this, he selected a number of constants for aqueous and ethyl alcohol solutions (due to Goldschmidt). In reply to this claim, Burkhardt (28) pointed out that the list of acids in question contained ortho-substituted benzoic acids, which had long been recognized to behave abnormally and therefore should be omitted from a general discussion (compare the findings of Wooten and Hammett (174)). A fuller review of dissociation constants of organic acids in

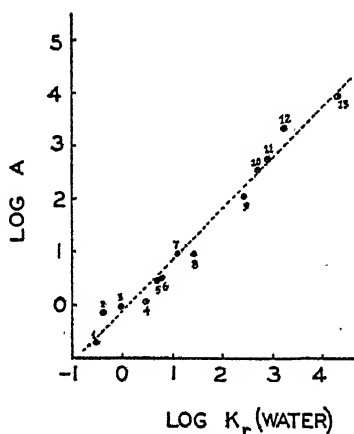


FIG. 2. Plot of $\log A$ against $\log K_r$ (water) for a number of acids. 1, acetic acid; 2, phenylacetic acid; 3, benzoic acid; 4, formic acid; 5, *m*-nitrobenzoic acid; 6, *p*-nitrobenzoic acid; 7, salicylic acid; 8, 3,5-dinitrobenzoic acid; 9, *o*-nitrobenzoic acid; 10, 2,4-dinitrobenzoic acid; 11, dichloroacetic acid; 12, trichlorobutyric acid; 13, trichloroacetic acid.

water and in methyl and ethyl alcohols was made later by Wynne-Jones (177), who postulated that dissociation constants will not present the same sequence from solvent to solvent, on account of the varying transfer energies of acids arising from the differing electrostatic conditions in each solvent. From electrostatic considerations he arrived at a relationship connecting dissociation constants in different solvents, and he showed that, for each of the acids under examination, a straight line was given when the values of $\log K_r$ (i.e., the logarithmic function of the ratio of the dissociation constant of the acid in question to that of benzoic acid, employed as reference) relating to the three solvents were plotted against the reciprocals of the dielectric constants of the solvents. One aim of the relationship was to provide a means of arriving at a satisfactory

comparison of acid strengths, and Wynne-Jones advocated that, in theoretical discussions, his "intrinsic strengths" (A) should be employed; these values refer to a theoretical solvent of infinite dielectric constant and are obtained from the graph by extrapolation, the intercept on the dissociation constant axis giving $\log A$. It is significant, however, that the values of A present the same sequence as that provided by K_{th} data for the same acids in water (see figure 2), and it is therefore not proved that dissociation constants of acids in water are likely to give an ambiguous relative order.

Lately, Minnick and Kilpatrick (103a) have recorded the relative strengths of a series of acids in water, methyl alcohol, and ethyl alcohol, which give further support for Wynne-Jones' relation (the lack of success experienced with data for certain water-dioxane mixtures seems to indicate that the applicability of the relationship is limited to solvents of dielectric constant > 25). An unaltered sequence of strengths is preserved in all three solvents, the results for *o*-chlorobenzoic acid being excluded, and, again, the intrinsic strengths are in qualitative agreement with the constants for aqueous solutions. It was shown, also, that the strengths of acids in two solvents of equal dielectric constant were the same.

In this connection it should be noted that Wooten and Hammett (174) have shown that with meta- and para-substituted benzoic acids the values of $\log K$, for butanol and water when plotted yield a straight line (actually, these workers believe that their results as a whole are best interpreted along the lines already discussed by Schwarzenbach and Egli (153a), who take into account, not only the dielectric constant of the solvent for the acid, but the distance separating the reacting group and the substituent and the component of the group dipole acting in this direction). Furthermore, the data provided by Halford (73), Bright and Briscoe (26), and Hixon (67) for alcoholic solutions, and by Griffiths (70) for chlorobenzene solutions (obtained by an indicator method) give, in each case, an order which is precisely the same as that derived from aqueous solutions (after excluding systems which are recognized as abnormal); and Kolthoff, Lingane, and Larson (113a) go so far as to predict the dissociation constants of acids in alcohols from a knowledge of the constants for aqueous solutions.

Apart from this, Wynne-Jones' relationship serves simply to relate K with dielectric constant, although it is known that changes in dielectric constant (and viscosity) do not wholly explain the difference in behavior of electrolytes in passing from solvent to solvent. The factor of chemical affinity, differing vastly with each solvent, is quite important; this point has already been made elsewhere by Hartley *et al.* (89), Hovorka and Simms (93), and others. Bound up with this matter is the problem of

true solvent correction, and until this has been elucidated, the strengths in non-aqueous solutions will not be determined (conductimetrically) with an accuracy approaching that which obtains with aqueous solutions.

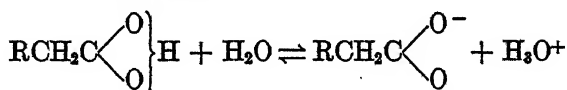
Meantime, in defense of the practice of basing theoretical discussion on a consideration of the relative strengths of acids and bases in water, it may be said that here the solvent possesses a high dielectric constant, and consequently the other factors affecting electrolytic dissociation are rendered comparatively less important; moreover, these are not likely to lead to complications where electrolytes of similar character are being considered. Actually, in any discussion in organic chemistry the acids under review are always of the same type, so that their strengths should be influenced consistently by various factors (13, 174, 170a). The only exceptions are likely to be found in acids containing substituents that affect the strength by some interaction in space, the influence of which may be governed abnormally by the magnitude of the dielectric constant (certain ortho-substituted benzoic acids belong to this category). It has become apparent from the available evidence that, when these systems are excluded, both "intrinsic strengths" and the approximate strengths recorded for various acids in non-aqueous solvents fall into the same sequence as the thermodynamic dissociation constants of these acids in water.

IV. THE EFFECT OF CONSTITUTION ON DISSOCIATION CONSTANTS

A. Generalizations

Ostwald's extensive measurements on carboxylic acids made it clear that substitution of certain groups or atoms gives rise to an increase of strength, whereas other groups lead to a diminution; these were the groups or atoms which had come to be regarded as possessing negative and positive characteristics, respectively. Also, it became evident that the influence of a group was to a great extent determined by its proximity to carboxyl; Wegscheider (170) actually calculated factors representing the influence of the common groups at different positions along the saturated aliphatic chain.

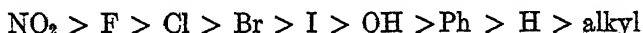
The ionic dissociation of an acid, e.g., of a substituted acetic acid, is governed by the following equilibrium,



Thus, when a substituent is introduced into an acid, the influence of the substituent relative to that of hydrogen is expressed by the extent to which the equilibrium is displaced in one direction or the other. When

the substituent has the effect of bringing the electrons of the hydrogen-oxygen linkage more under the control of the oxygen, it leads to an enhancement of acid strength, and, conversely, when the substituent causes the opposite movement of electrons, it creates a diminution of strength.

In the substituted acetic acids the extent to which the polarity of the substituent group influences the dissociation constant of the acid is analogous to its effect on the dipole moment (μ) of the corresponding substituted methane. The electron-attractive or electron-repulsive nature of groups is identified with the amount of restraint exercised by the groups over their covalency electrons, and common substituents give the following diminishing order:



The effect of this restraint is transmitted through the molecule and through space, and is likened to electrostatic induction. Flürscheim (61) recognized such an effect, and it has been discussed more precisely in recent years by Lapworth, Robinson, and Ingold, independently, although we are indebted to Lewis (118) for its original electronic interpretation. Throughout this paper the terminology of Ingold is employed; consequently this polar influence in question is referred to as the inductive effect (represented as I), electron repulsion, $\text{R} \rightarrow \text{C}$, is given a positive sign, and electron attraction, $\text{R} \leftarrow \text{C}$, is given a negative sign.

In unsaturated conjugate systems there occurs, in addition to the electronic displacement of inductive type, a migration of electrons involving covalency changes as postulated by Lowry (123). It is now understood that this second effect is partly of permanent character and, therefore, like the inductive effect, is reflected in the dipole moment; this permanent component is termed the mesomeric effect (M) and is the outcome of the resonance of the molecule. The total effect, consisting of the permanent and time-variable factors (the latter being brought out on attack of reagents and called the electromeric effect (E)), is designated the tautomeric effect (T) and is represented by curved arrows (\curvearrowright).

In interpreting the influence of a substituent in a given position, in benzoic acid, for instance, the changes resulting from the operation of both electronic disturbances must be taken into account.

Full details of the different polar influences, together with accounts of the implications of the conception of quantum-mechanical resonance in theoretical organic chemistry are to be found in recent summaries (147, 96, 167, 168, 104, 142). These principles are assumed in this discussion of the effects of substituent groups on the strengths of acids, which are supported by data for phenols and bases (all the dissociation constants are assembled in the appendix). In the text of the discussion it is fre-

quently more convenient to give the strengths of acids in terms of the unsubstituted acid as unity, i.e., K/K_u . Where the actual dissociation constants are quoted, the values have been multiplied by 10^5 unless otherwise stated, and refer to aqueous solution at 25°C.

B. The influence of alkyl groups²

Alkyl groups usually exhibit a weak electron-repulsive character (+I); this has been amply demonstrated in various reactions. In the paraffins, however, methyl fails to reveal any polar influence, as shown by the negligible dipole moments of these compounds; this gives ground for the belief that the inductive effect of the alkyl group arises from a stimulation produced by the rest of the molecule (96). When alkyl is directly attached to the aromatic nucleus or to conjugate unsaturated systems generally, electromeric displacements occur; actually this disturbance and the inductive effect both contribute to the dipole moment of toluene.³

TABLE 2
Strengths of methyl-substituted aromatic acids

| | K/K_u^* | | |
|-------------------|------------|------------|------------|
| | <i>o</i> - | <i>m</i> - | <i>p</i> - |
| Benzoic..... | 1.97 | 0.87 | 0.68 |
| Cinnamic..... | 0.87 | 1.00 | 0.75 |
| Phenylboric†..... | 0.13 | 0.71 | 0.51 |

* K_u always refers to each appropriate parent acid.

† The tabulated data for substituted phenylboric acids (and phenols) contained in this Section refer to aqueous alcoholic solutions.

The strengths of methyl-substituted aromatic acids reveal that the influence of methyl in the three positions of the nucleus follows the order *o*- and *p*- > *m*- (the abnormal *o*-toluic acid is excluded), as will be seen from table 2. The more effective the substituent the lower the acid strength becomes, and the actual order obtained is a natural consequence of the operation of electromeric displacements from the ortho- and para-positions. A marked diminution of influence is observed in passing from *p*-toluic to *p*-tolylacetic acid (K/K_u , 0.87), and very little further decrease in *p*-methyl- β -phenylpropionic acid (K/K_u , 0.94), although substitution of

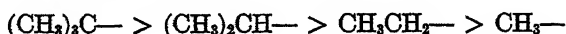
² The strengths of aliphatic acids are not discussed here, since they are best dealt with in the light of considerations given in later pages.

³ Since revision of this article values for the dipole moments of alkylbenzenes and alkylcyclohexanes have been published by Baker and Groves (J. Chem. Soc. 1939, 1147), and discussed in a further paper dealing with the polar effects of alkyl groups (BAKER: J. Chem. Soc. 1939, 1150).

p-methyl in cinnamic acid causes a fall nearly as marked as in benzoic acid; this latter change must be attributed to the existence of the conjugate system, which permits the tautomeric transfer of electrons.

Similar conclusions may be drawn from the strengths of methyl-substituted anilines (75), dimethylanilines (36), and benzylamines (30). It must be remembered, of course, that the relative order of strengths of the bases will be the converse of that observed with acids.

Increase of the inductive effect is brought about by extension of the *n*-alkyl chain (110), and also upon progressive substitution of methyl by further methyl groups giving the sequence (96)



It is noteworthy, however, that the introduction of these homologous groups into aromatic acids indicates the existence of modifying factors; this will be seen from the relative strengths (8) cited below.

| ACID | K/K_u | | | |
|---------------------------------------|---------------|------------------------|-------------------------------------|--------------------------------------|
| | CH_3 | C_2H_5 | <i>iso</i> - C_4H_7 | <i>tert</i> - C_4H_9 |
| <i>p</i> -Alkylbenzoic acid..... | 0.68 | 0.71 | 0.71 | 0.63 |
| <i>p</i> -Alkylphenylacetic acid..... | 0.87 | 0.87 | 0.83 | 0.78 |

Thus the polar influences of the alkyl substituents, in the benzoic acid series, at least, present a distinctly abnormal order, *viz.*, *tert*-butyl > methyl > ethyl \approx isopropyl > hydrogen. (It must be borne in mind that this is the order of polar effects, and not of acid strengths.) Anomalies of this kind have been discussed by Baker and Nathan (9), who visualize an electron release of mesomeric type arising from the H- α -C bond, which functions in addition to the inductive effect and decreases in the order methyl \gg ethyl > isopropyl. It is claimed that this operates only when alkyl is attached to a conjugate system, and that it has its origin in the tendency for electron displacements from the duplet forming the C-H bond in methyl or substituted methyl, *i.e.*, CH_3CH_2- or $(\text{CH}_3)_2\text{CH}-$; consequently no such effect is associated with *tert*-butyl. This influence when combined with the inductive effect (possessing the same sign but presenting the converse order of magnitudes) might easily lead to a partial or total inversion of the effects of the alkyl groups in question. The strengths of the *p*-alkyl groups quoted here are, therefore, quite in harmony with the Baker-Nathan postulate; it is scarcely to be expected that the anomaly will be detectable in the phenylacetic acid system. The presence of a marked modifying influence in the benzoic acid system only will account for the fact that the differences in strength

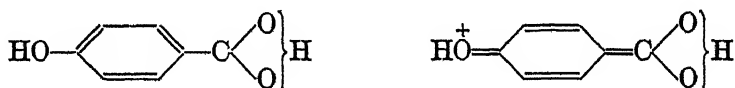
between various alkylbenzoic acids are no greater than those between the alkylphenylacetic acids.

Anomalous behavior of this kind was first observed in the nuclear substitution of *p*-alkyltoluenes which, contrary to expectation, yield a preponderance of the 2-derivative. Kinetic measurements have also furnished examples of this feature, the most recent being provided by studies of the acid-catalyzed prototropy of phenyl alkyl ketones (55) and of the alkaline hydrolysis of saturated aliphatic esters (57).

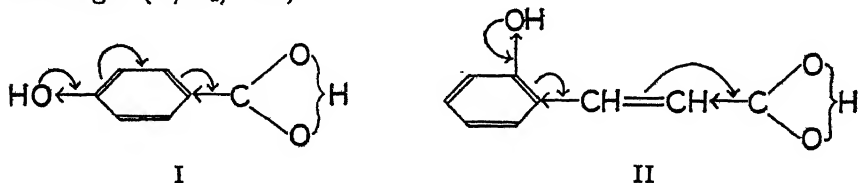
C. The influence of hydroxyl and alkoxyl groups

The hydroxyl group has a distinct attraction for electrons ($-I$), but in addition it is capable of releasing unshared electrons from the oxygen atom by the tautomeric mechanism ($+T$) where the system is favorable; thus, for instance, phenols and phenolic ethers give ortho- and para-derivatives on nuclear halogenation and nitration.

In saturated acids substitution of hydroxyl introduces a $-I$ effect only; thus glycolic acid (K/K_u , 8.3) and mandelic acid (K/K_u , 8.0) are stronger than acetic and phenylacetic acids, respectively. Likewise, when hydroxyl occupies the meta-position of benzoic acid, K is increased (K/K_u , 1.32), but *p*-hydroxyl, on the other hand, brings about a fall in strength (K/K_u , 0.46), because here (see formula I) the powerful $+T$ effect (having its origin in resonance between the following structures) successfully opposes $-I$.

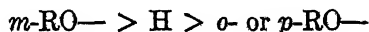


For a similar reason *o*-hydroxycinnamic acid (II) is weaker than the parent cinnamic acid (K/K_u , 0.67), although the meta-substituted acid is stronger (K/K_u , 1.10).



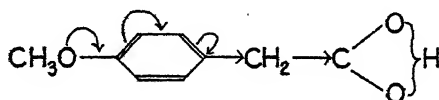
Salicylic acid, which exhibits abnormality, will be discussed later.

The influence of alkoxyl is naturally similar to that of hydroxyl. The order of strengths



is observed in the methoxybenzoic (excluding the ortho-acid), methoxyphenylacetic, methoxy- β -phenylpropionic, methoxycinnamic, and ethoxy-

phenylboric series, as will be seen from table 3. It has been pointed out elsewhere (49, 46) that the inclusion of phenylacetic and β -phenylpropionic acids would not perhaps have been anticipated, since the transmission of an electromeric effect, as such, is rendered impossible by the intervening methylene linkage (or linkages). The explanation given is that the electromeric displacements initiated by methoxyl proceed to the *p*-(or *o*)-carbon atom, whence the influence of the resulting negative charge is propagated inductively to the carboxyl (III). The substituent is exerting what Robinson (148) has described as "virtually a relayed general or inductive effect."



III

It is noteworthy that the polar influences are most pronounced in the benzoic and cinnamic acids; this is a generalization which applies to all substituent groups and can be attributed to the existence, in those acids, of conjugate systems which greatly facilitate the transfer of polar influences. Also, it is seen that as the substituted benzene nucleus is removed further from the carboxyl, the effect of methoxyl becomes relatively smaller; this is noticeable elsewhere, in the relative effects of other substituents upon benzoic, phenylacetic, and β -phenylpropionic acids.

The contrasting influences of *m*- and *p*-methoxyl (and ethoxyl) groups have been demonstrated in the velocity data for various side-chain reactions, such as the hydrolysis of benzyl bromides (116) and of benzoic and cinnamic esters (111) and the stabilities of potassium hydroxamates (26a); also in the basic strengths of the anilines (75), the dimethylanilines (36), and the benzylamines (30) (see appendix).

A further significant observation is forthcoming from a comparison of the strengths of the hydroxy and corresponding methoxy acids so far determined. Contrary to expectation, methyl, when it displaces hydrogen of the hydroxyl group, causes an *increase* in acid strength (see table 4). On precedent, a definite weakening of the acid would be anticipated upon introduction of methyl, which is regarded as possessing a $+I$ effect. It must be borne in mind, however, that the evidence which indicates this polar influence of methyl refers essentially to methyl attached to carbon. Indeed, it now appears that the sign of the inductive effect is altered when methyl is linked to oxygen, and there exists other evidence to show that the reversal of the normal polar effect is characteristic of

methyl in the methoxyl group. It has been shown by Groves and Sugden (72) that phenol possesses a mesomeric moment (1.12) far in excess of that of anisole (0.40); again, it is well known that anisole is attacked by electrophilic reagents far less readily than phenol. Actually, nothing is known of the genesis of the inductive effect of methyl except that its polarity is impressed upon it by the group to which it is attached, and

TABLE 3
Influence of alkoxyl groups on dissociation

| | K/K_u | | |
|---|---------|------|------|
| Methoxybenzoic acid..... | 1.29 | 1.30 | 0.54 |
| Methoxyphenylacetic acid..... | | | 0.89 |
| Methoxy- β -phenylpropionic acid..... | 0.72 | 1.01 | 0.94 |
| Methoxycinnamic acid..... | 0.94 | 1.15 | 0.79 |
| Ethoxyphenylboric acid..... | 0.46 | 1.55 | 0.31 |

TABLE 4
*Strengths of hydroxy- and methoxy-substituted acids**

| ACID | K/K_u |
|-------------------------------------|---------|
| Glycolic acid..... | 15 |
| Methoxyacetic acid..... | 33.5 |
| <i>m</i> -Hydroxybenzoic acid..... | 8.3 |
| <i>m</i> -Methoxybenzoic acid..... | 8.1 |
| <i>p</i> -Hydroxybenzoic acid..... | 2.9 |
| <i>p</i> -Methoxybenzoic acid..... | 3.38 |
| <i>o</i> -Hydroxycinnamic acid..... | 2.44 |
| <i>o</i> -Methoxycinnamic acid..... | 3.45 |
| <i>p</i> -Hydroxycinnamic acid..... | 4.00 |
| <i>p</i> -Methoxycinnamic acid..... | 4.21 |

* See references 140, 22, 141, and the appendix.

Ingold (96) states that, although "alkyl groups generally function as feebly repelling groups, the possibility of the other type of behaviour can be foreseen."

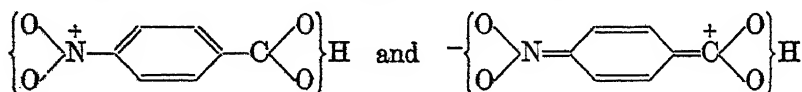
The change brought about by substituting higher alkyl groups in hydroxy acids is also noteworthy; measurements show that, although introduction of alkyl into glycolic acid always greatly enhances K , the

effect diminishes as the group extends (141) (compare the effects of different alkoxy groups upon halogenation and nitration of the benzene nucleus (105, 146, 31)).

A number of data are available for acids bearing the phenoxy group. The sequence of strengths for the substituted benzoic acids is $m\text{-C}_6\text{H}_5\text{O}- > \text{H} > p\text{-C}_6\text{H}_5\text{O}-$ (see appendix), which is the same as that obtained with methoxybenzoic acids (in this connection it should also be noted that p -phenoxyphenylboric acid is much weaker than the unsubstituted phenylboric acid (19)). It is interesting, however, that in the para-position phenoxy reduces K more effectively than does methoxy, whereas in the meta-position it leads to a comparatively greater strength; this latter feature doubtless arises from the inherent electron-attractive character of phenyl as opposed to the electron-repulsion of methyl (see page 169). On the other hand, in the p -phenoxy group the ambipolar tautomeric character of phenyl ($\pm T$), now capable of exerting itself, apparently gives rise to a greater accession of electrons towards the nucleus than does the inductive effect of methyl. The order $m\text{-C}_6\text{H}_5\text{O}- > \text{H}$ is due to the operation of the inductive effect alone; for the same reason (and to a greater degree) phenoxyacetic acid (K/K_u , 42) is very much stronger than acetic acid and, naturally, stronger than methoxyacetic acid (K/K_u , 18.6); this is in harmony with the observation (117) that, in aromatic substitution, the directive power of phenoxy is small by comparison with that of methoxy.

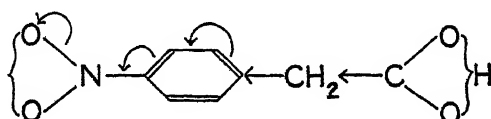
D. The influence of the nitroxyl group

The nitro-substituent is powerfully meta-directing in aromatic substitution, indicating a pronounced electron-attractive nature, and consequently it is to be expected that this substituent should increase considerably the strength of an organic acid. For aromatic acids the order of falling strengths is $p\text{-NO}_2 > m\text{-NO}_2 > o\text{-NO}_2 > \text{H}$ (excluding the ortho-substituted benzoic acid), as will be seen from table 5. The inductive effect, alone, should lead to the order of strengths $m- > p-$, but the reverse is actually the case, partly because electromeric displacements ($-T$) occur from the para-position. Numerous examples of the same feature are to be found in the data for reaction velocities of side-chain processes (172) and for classical dissociation constants of phenols (91) and anilines (120a). This additional effect is the outcome of resonance between benzenoid and quinonoid structures (49); with p -nitrobenzoic acid, for example, the following represent the unperturbed structures:



This is in contrast to the resonance obtaining in *p*-hydroxybenzoic acid, where the movement of electrons is in the opposite direction (see page 171).

The tautomeric effect is capable of being relayed to some extent through a saturated hydrocarbon chain by the mechanism indicated in formula IV, as shown by *p*-nitrophenylacetic and *p*-nitro- β -phenylpropionic acids, which preserve the normal order (*cf.* the effect of *p*-methoxyl).



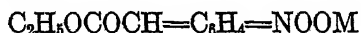
IV

It is remarkable that the relative difference between meta- and para-substituted acids is greater in the phenylacetic and β -phenylpropionic acid series than in the benzoic acid series; this is contrary to anticipation,

TABLE 5
Strengths of nitro-substituted acids

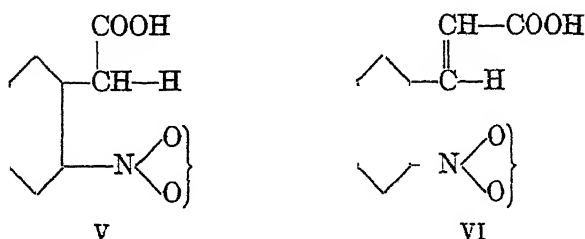
| SYSTEM | K/K_u | | |
|------------------------------------|------------|------------|------------|
| | <i>o</i> - | <i>m</i> - | <i>p</i> - |
| Benzoic acid..... | 107 | 5.19 | 6.00 |
| Phenylacetic acid..... | 2.03 | 2.21 | 2.89 |
| β -Phenylpropionic acid..... | 1.44 | | 1.54 |
| Cinnamic acid..... | 1.94 | 2.08 | 2.46 |
| Phenylboric acid..... | 2.84 | 35.0 | 49.7 |

as the tautomeric effect should be far more effective in the latter. The explanation advanced (43) is that in the para series hydrogen ion arises to some extent from the methylene group; this is possible in view of the well-known reactivity of methylene in phenylacetic acid (and in like compounds), and the isolation, by Opolski and Zwislocki (137), of salts of the postulated formula



Moreover, it is noteworthy that the ortho-substituted acids, unlike the para-substituted acids, are not stronger than the meta-substituted acids, although electromeric disturbances should operate from the ortho-position as easily as from the para-position, so as to facilitate ionization of the acid. The suggestion offered by Dippy and Lewis (45, 46) is that nitroxyl in the ortho-substituted acids (phenylacetic (V), β -phenylpropionic, and cinnamic (VI)) is capable of chelating with hydrogen of the methylene

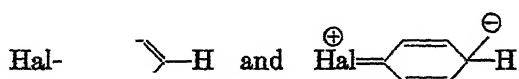
group along the lines proposed by Sidgwick and Callow (156) for *o*-nitrotoluene.



The effect of this chelation is to oppose ionization.

E. The influence of halogens

The inductive effects of the halogens ($-I$) present the sequence $F > Cl > Br > I$, and the old-established strengths of the halogenoacetic acids are consistent with this. When halogen is attached to the aromatic nucleus, however, its polar effect is considerably modified by an influence of the tautomeric type which diminishes from F to I , thus presenting the same relative order as the inductive effects but possessing the opposite sign. This modifying factor was first recognized by Baddeley and Bennett (4), and it is now generally believed to be a mesomeric effect arising from resonance between benzenoid and quinonoid forms (179, 96), although agreement has not been reached regarding the genesis of this polarization of the aromatic nucleus. Whereas Ingold and Branch attribute it to resonance between structures such as



Bennett and coworkers (14) state that the dipolar unperturbed structure should not involve an actual increase of covalency between halogen and nuclear carbon, if the order $F > \dots > I$ is to be preserved. They overcome the difficulty by proposing the following dipolar structure,



although they admit of a distinct polarizability of the halogen-carbon bond, diminishing in the order $I > \dots > F$ (cf. 96, 148). Recently Bird and Ingold (20) have postulated this sequence for the total polarizability effect, which appears to be prominent in aromatic substitution processes (Baker (6) has also been led to this order for the electromeric effects).

The foregoing conflicting influences ascribed to the halogen substituents are in accord with the well-known fact that the halogens, although ortho-

para orienting, deactivate the aromatic nucleus (this has been discussed by Bird and Ingold, who have recorded the comparative rates of nitration of monohalogenobenzenes by acetyl nitrate at 18°C.: H, 1; F, 0.15; Cl, 0.03; I, 0.18), and with various dipole moment measurements (most significant in this connection is the sequence of mesomeric moments published by Groves and Sugden (71), *viz.*, C_6H_5F , 1.00; C_6H_5Cl , 0.97; C_6H_5Br , 0.89; C_6H_5I , 0.87).

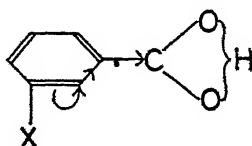
For simplicity the polar effects associated with halogens attached to the benzene ring may be represented as $-I + M (+E)$; the relative

TABLE 6
Effect of halogen substitution upon the dissociation of organic acids

| POSITION OF SUBSTITUENT | VALUES OF K/K_u | | | |
|----------------------------|-------------------|------|------|------|
| | F | Cl | Br | I |
| Benzoic acid series | | | | |
| <i>o</i> - | 8.61 | 18.2 | 22.3 | 21.9 |
| <i>m</i> - | 2.18 | 2.36 | 2.46 | 2.25 |
| <i>p</i> - | 1.15 | 1.68 | 1.71 | |
| Phenylacetic acid series | | | | |
| <i>o</i> - | | 1.76 | 1.81 | 1.88 |
| <i>m</i> - | | 1.48 | | 1.42 |
| <i>p</i> - | 1.16 | 1.32 | 1.33 | 1.36 |
| Phenylboric acid series | | | | |
| <i>o</i> - | | 7.10 | | |
| <i>m</i> - | 5.58 | 6.85 | 7.41 | |
| <i>p</i> - | 1.86 | 3.20 | 3.68 | |
| Phenol series | | | | |
| <i>o</i> - | 13.4 | 31.9 | 30.6 | 28.5 |
| <i>m</i> - | 4.72 | 15.3 | 13.7 | 12.2 |
| <i>p</i> - | 0.81 | 4.13 | 4.13 | 6.84 |

influence of these factors upon a particular reaction depends on the system, the nature of the attacking reagent, and external conditions. Thus it happens that halogens in aromatic combination frequently fail to present the inductive order, and sometimes reveal a complete inversion of this order. From the strengths of aromatic acids and of phenols it is seen that, although the inductive effect is the predominant factor (the dissociation constants, with one exception, are distinctly higher than those of the unsubstituted compounds), there is superimposed upon this the opposing mesomeric effect (see table 6). The net polar effect arising from this

combination of influences has produced, in these acids, partially or completely inverted sequences throughout (the net result of these opposing factors is easily appreciated by reference to the diagrammatic representation by Dippy and Lewis (43)). It will be noted that the *o*- and *p*-fluoroacids (and *o*- and *p*-phenols) are markedly weaker than the others, indicating a very considerable mesomeric effect in the case of fluorine. Actually this effect appears to predominate in *p*-fluorophenol, the dissociation constant of which is lower than that of phenol. A further important observation is that irregularities extend to the *m*-halogenoacids; the explanation given (43) is that the disturbance, virtually electromeric, is relayed inductively by the following mechanism (taking, for example, the benzoic acid system (VII)):



VII

Furthermore, it seems, from the data on phenylacetic acid, that the mesomeric effect can be transmitted through a saturated carbon chain (*cf.* the effect of methoxyl).

Comparable data are provided by the halogenoanilines and halogeno-dimethylanilines (see appendix), where a complete inversion is observed. Additional evidence of the irregularity of the effects of halogens attached to benzene is forthcoming from numerous measurements on reaction velocity (see reference 4 for a summary).

F. The influence of ethenyl and phenyl groups

When the vinyl and phenyl groups are introduced into an aliphatic acid, there is an appreciable increase in strength, as will be seen from the following K/K_* figures:

| VINYLAACETIC ACID $\text{CH}_2=\text{CHCH}_2\text{COOH}$ | PHENYLACETIC ACID $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ | DIPHENYLACETIC ACID $(\text{C}_6\text{H}_5)_2\text{CHCOOH}$ |
|---|---|--|
| 2.55 | 2.78 | 6.55 |

This leads inevitably to the conclusion that the ethenyl and phenyl groups possess an intrinsic attraction for electrons (60, 61, 3, 122, 96, 131); for the sake of simplicity Dippy and Lewis (44) refer to this permanent influence as an inductive effect ($-I$). Dipole moment measurements

verify the existence of such an effect; in the case of vinyl the following data (in Debye units) due to Højendahl (161) may be cited as evidence:

| | | | | | |
|--------------------|------|----------------------------|------|-----------------------------|------|
| Vinyl bromide..... | 1.48 | Allyl bromide..... | 1.93 | Allyl chloride..... | 1.97 |
| Ethyl bromide..... | 2.09 | <i>n</i> -Propyl bromide.. | 2.15 | <i>n</i> -Propyl chloride.. | 2.11 |

Again, analysis of the dipole moments of substituted benzenes has demonstrated that the aromatic nucleus, on account of its polarizable character, makes a contribution to the measured moment (159, 15).

Although it has still to be understood precisely how this polarization arises, it doubtless has its origin in the unsaturated nature of the groups in question. It is certainly significant that saturation of acids bearing these groups leads to a marked diminution in dissociation constant (see

TABLE 7

Effect of ethenyl and phenyl groups upon the dissociation of acids

| | $10^4 K$ |
|--|-------------------|
| Vinylacetic acid, $\text{CH}_2=\text{CHCH}_2\text{COOH}$. | 4.62 |
| Butyric acid, $\text{CH}_3(\text{CH}_2)_2\text{COOH}$ | 1.50 |
| Allylacetic acid, $\text{CH}_2=\text{CH}(\text{CH}_2)_2\text{COOH}$. | 2.11 ₅ |
| Valeric acid, $\text{CH}_3(\text{CH}_2)_3\text{COOH}$ | 1.38 |
| Benzoic acid, $\text{C}_6\text{H}_5\text{COOH}$ | 6.27 |
| Cyclohexanecarboxylic acid, $\text{C}_6\text{H}_{11}\text{COOH}$. | 1.34 |
| Phenylacetic acid, $\text{C}_6\text{H}_5\text{CH}_2\text{COOH}$ | 4.88 |
| Cyclohexylacetic acid, $\text{C}_6\text{H}_{11}\text{CH}_2\text{COOH}$... | 2.36 |

table 7). It will be noticed that the acids containing the cyclohexyl group possess strengths very similar to those of the fatty acids.

Comparable results have been obtained with bases upon saturation of the aromatic nucleus, as will be seen from the following data for pK_H obtained by Hall and Sprinkle (75): aniline, 4.6; cyclohexylamine, 10.61; methylamine, 10.64; also *cf.* pyridine, 5.21, and piperidine, 11.31.

It should also be noted that the introduction of a triple bond enhances the strength of an acid much more than does the double bond; this is illustrated by the constants given in table 8. The dipole moment data of Wilson and Wenzke (173) for compounds containing triple bonds likewise indicate that the greater the degree of unsaturation the more pronounced the intrinsic attraction for electrons becomes.

There is ample evidence to show that the so-called inductive effect of

the vinyl and phenyl groups can be transmitted along a saturated carbon chain as far as the third member. In table 9 the reference acid in each case is the corresponding saturated acid. Similar conclusions can be drawn from the relative strengths of phenyl-, benzyl-, and phenylethyl-boric acids (24, 19), and of the phenyl-substituted aliphatic primary amines (30) (see appendix).

When the vinyl and phenyl groups are present in a conjugate unsaturated system, however, a second factor is introduced. It is recognized that these groups, by virtue of their available electrons, are capable of being concerned in electromeric displacements in either direction according to

TABLE 8

Effect of a triple bond upon the dissociation of organic acids

| | 10 ³ K |
|--|-------------------|
| Propionic acid, CH ₃ CH ₂ COOH..... | 1.33 |
| Acrylic acid, CH ₂ =CHCOOH..... | 5.56 |
| Crotonic acid, CH ₃ CH=CHCOOH..... | 2.03 |
| Tetrollic acid, CH ₃ C≡CCOOH..... | 222.8 |
| Phenylpropionic acid, C ₆ H ₅ C≡CCOOH. | 590 |

TABLE 9

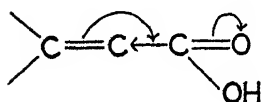
Transmission of effect of vinyl and phenyl groups along a carbon chain

| | K/K _u |
|---|------------------|
| Acrylic acid, CH ₂ =CHCOOH..... | 4.17 |
| Vinylacetic acid, CH ₂ =CHCH ₂ COOH..... | 3.08 |
| Allylacetic acid, CH ₂ =CH(CH ₂) ₂ COOH... | 1.53 |
| Phenylacetic acid, C ₆ H ₅ CH ₂ COOH..... | 2.78 |
| β-Phenylpropionic acid, C ₆ H ₅ (CH ₂) ₂ COOH. | 1.67 |
| γ-Phenylbutyric acid, C ₆ H ₅ (CH ₂) ₃ COOH... | 1.17 |

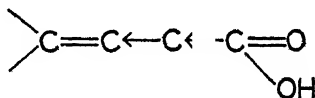
the demand ($\pm T$). This is strikingly illustrated in the relative stabilities of cyanohydrins recorded by Lapworth and Manske (115); phenyl when directly linked to carbonyl acts in the same sense as methyl but causes a 42-fold change in the constant, whereas when phenyl is not conjugated with carbonyl, as in methyl benzyl ketone, no appreciable difference in the constant is noted.

This combination of polarization and polarizability effects gives an interpretation to a number of other features apparent in the present data for olefinic and phenyl-substituted acids. In the first place, on comparing acrylic, vinylacetic, and allylacetic acids, it is seen that there is a gradual fall in strength, but the difference between the α,β - and β,γ -unsaturated acids is less than that between the β,γ and γ,δ acids. The operation of the $-I$ effect alone should lead to the order $\alpha,\beta \gg \beta,\gamma > \gamma,\delta$ (comparable

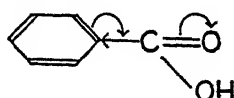
to that for halogenated aliphatic acids), but actually in the α,β -acid an opposing electromeric disturbance operates which serves to reduce the dissociation constant (see VIII), even to the extent of producing a different order of strengths among the acids in some instances (*cf.* 99); where the double bond and carboxyl are not included in a conjugate system (IX), only one influence is exerted. A similar reason can be advanced for the anomaly of the first member of the phenyl-substituted series of acids, namely, benzoic acid (X); the difference between the dissociation constants of phenylacetic and β -phenylpropionic acids suggests a constant for benzoic acid far in excess of that actually observed (see appendix).



VIII



IX



Examination of the relative strengths of aniline, benzylamine, and β -phenylethylamine discloses a similar feature (appendix).

It has been shown beyond doubt (99) that for *n*-pentenoic and *n*-hexenoic acids the order of strengths is actually $\beta,\gamma > \alpha,\beta > \gamma,\delta$. Evidence of similar significance is provided by the following hydroaromatic acids (32, 149) (K_u relates to the parent saturated acid):

| ACID | K/K_u |
|---|---------------|
| Δ^1 - and Δ^2 -tetrahydrobenzoic acid..... | 1.60 and 2.24 |
| Δ^1 - and Δ^2 -cycloheptenecarboxylic acid..... | 0.76 and 2.20 |

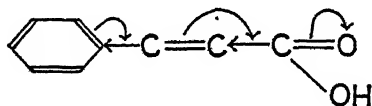
These are instances of the condition indicated above, where the tautomeric effect is great enough to affect the order of strengths. The alternation of dissociation constants in a series, emphasized by earlier workers, is merely incidental and has no meaning beyond that given here.

The influence of alkyl substituents in olefinic acids is much more pronounced than in saturated acids, and this can be attributed to the fact that the system containing the double bond is far more impressionable than one with a saturated carbon chain. Introduction of a methyl or ethyl group into acrylic acid causes the strength to fall by more than one-half, while a second methyl group brings about a further striking diminution of strength, as will be seen from the following results:

| | K/K_u | | |
|-----------------------|-----------------|-------------------------------|---------------------------------|
| | CH ₃ | C ₂ H ₅ | (CH ₃) ₂ |
| Acrylic acid..... | 0.37 | 0.36 | 0.14 |
| Vinylacetic acid..... | 0.69 | 0.68 | 0.56 |

It is natural, of course, that the influence of alkyl should be less marked in the non-conjugate system.

Phenyl brings about reduction of acid strength when situated in the β -position of an α,β -olefinic acid, e.g., cinnamic acid (K/K_u , 0.66). Doubtless the tautomeric effect of phenyl preponderates here (XI).



XI

In the α -position, however, phenyl has the net effect of enhancing K , as now its inductive influence alone operates (atropic acid: K/K_u , 2.57 (140)).

In contrast to the evidence provided by the phenyl-substituted acids discussed above, there are instances of reactions where the polar influence of phenyl appears to be subordinate to that of methylene; the best known include the ortho-para substitution of diphenylmethane, the relative stabilities of cyanohydrins (115), where introduction of a terminal phenyl group into acetone, methyl ethyl ketone, and methyl *n*-propyl ketone has scarcely any effect upon the thermodynamic constant, and the nitration of guaiacol benzyl ether (1), in which phenyl behaves as though it were conjugated with the aromatic ring in creating a recession of electrons from itself. Thus it is obvious that the individual influences associated with the polarization and polarizability of phenyl are exhibited in varying degree, the priority being determined by the system in which the group is situated and the nature of the reaction.

G. The ortho-effect

It is well known that introduction of one or two groups into the ortho-positions of a substituted benzene frequently leads to a marked retardation, or even a complete inhibition, of reaction. Outstanding, of course, are the classical works of Victor Meyer on the esterification rates of organic acids. It was pointed out by Meyer (129, 130) that the abnormality (referred to herein as the "ortho-effect") depends not so much upon the chemical character of the ortho-substituent as upon its size (although no consistent relationship between group size and resultant abnormality was apparent), and it was also shown that behavior was normal when the reacting group was separated from the benzene nucleus by one or more carbon atoms.

The relatively high strengths of ortho-substituted benzoic acids have

long been recognized, and this observation has lately been confirmed further by Dippy and Lewis (45) whose measurements are tabulated in table 10 (the constants for phenylacetic acids are included for purposes of comparison). An increase in strength is noted even in the case of substituents which usually have the effect of depressing the dissociation constant.

Meyer's interpretation of the ortho-effect was applied by Flürscheim (61) to explain these high dissociation constants. In modern terms this explanation assumes that in dilute aqueous solution, where the acid is in continuous contact with water, only the reassociation (reverse) process in the equilibrium

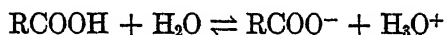
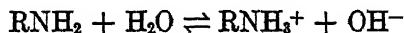


TABLE 10

Effect of various substituents on the dissociation of organic acids

| POSITION OF SUBSTITUENT | VALUES OF K/K_u | | | | | | |
|-------------------------------|-------------------|------|-------------------|------|------|------|-----------------|
| | CH ₃ | HO | CH ₂ O | Cl | Br | I | NO ₂ |
| Benzoic acid series | | | | | | | |
| <i>o</i> - | 1.97 | 15.9 | 1.29 | 18.2 | 22.3 | 21.9 | 107 |
| <i>m</i> - | 0.87 | 1.26 | 1.30 | 2.36 | 2.46 | 2.25 | 5.19 |
| <i>p</i> - | 0.68 | 0.44 | 0.54 | 1.68 | 1.71 | | 6.00 |
| Phenylacetic acid series | | | | | | | |
| <i>o</i> - | | | | 1.76 | 1.81 | 1.88 | 2.03 |
| <i>m</i> - | | | | 1.48 | | 1.42 | 2.21 |
| <i>p</i> - | 0.87 | | 0.89 | 1.32 | 1.33 | 1.36 | 2.89 |

will be affected by steric hindrance; retardation of this process, brought about by the blocking effect of the substituent, leads to an enhanced dissociation constant. Similar views when applied to the equilibrium



would demand an increase of basic strength in ortho-substituted anilines, for here again only the reverse change should be influenced unfavorably, but actually a marked *decrease* in strength is observed. Straightforward behavior is exhibited by the substituted benzylamines and *N, N*-dimethylanilines (appendix), although it is remarkable that the dimethylanilines should contrast with the anilines in this respect.

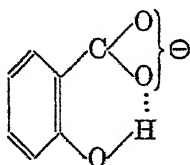
Very few di-ortho-substituted benzoic acids have been examined so

far; nevertheless it has become evident that introduction of the second substituent brings about a further large increase in strength.

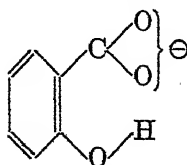
| | K/K_u |
|--|---------|
| 2,6-Dihydroxybenzoic acid (140)..... | 797 |
| 2,6-Dinitrobenzoic acid (157)..... | 1299 |
| 2-Methyl-6-nitrobenzoic acid (46)..... | 181 |

In a survey of the problem of the ortho-effect, Dippy, Evans, Gordon, Lewis, and Watson (42) have pointed out that apparent abnormality is observed in aromatic compounds possessing suitably placed substituents only when the reacting group is a powerful electron-donor, and, in support of this, certain reaction velocity data are cited. Therefore it appears that consideration of the bulk of the ortho-substituent fails to account entirely for the ortho-effect; doubtless, interaction of groups intervenes, and this frequently constitutes the major factor. Thus the present view is that interference with the process of reassociation of the ions of the acid may be effected both by group interaction in space and by bulk (geometrical) influence.

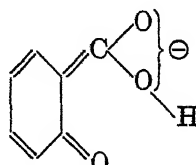
Probably the large bulk of the ortho-substituent is chiefly responsible for the high strengths exhibited by *o*-phenyl- and *o*-phenoxy-benzoic acids; it is seen, for example, that in passing from the latter acid to *o*-methoxybenzoic acid, simple alteration of the hydrocarbon radical causes K to fall to almost one-quarter of its value. On the other hand, the strength of salicylic acid is an order greater than that of *o*-methoxybenzoic acid or of acetylsalicylic acid; obviously the factor intervening here is not of geometrical character. To account for this, Branch and Yabroff (23) have postulated the formation of a hydrogen bond between the hydroxyl and carboxyl groups (compare Sidgwick and Callow's suggestion of chelation in ortho-substituted phenols (156)), whereby reassociation of anion and hydrion is inhibited. It will be seen from formula XII that the groups are favorably situated, and the resonance that renders the bond possible is facilitated by the electronic rearrangements occurring between XIII and XIV (unperturbed structures).



XII



XIII

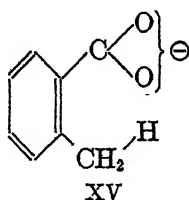


XIV

This concerns the anion (almost entirely) which will form such a bond more readily than the undissociated acid, since the electron-donating

atom here is actually charged. The further large increase in strength exhibited by 2, 6-dihydroxybenzoic acid has been attributed by W. Baker (10) to the formation of hydrogen bonds by both oxygens of carboxyl. Good support for the suggested chelation in phenolic compounds has been forthcoming from infrared absorption spectra (89a, 88a, 175a, 67a); the characteristic OH absorption is found to be absent in certain ortho-substituted phenols, such as salicylaldehyde, *o*-nitrophenol, and salicylic esters, and this is attributed to hydrogen bonding involving the hydroxyl group.

The view has been advanced (42) that a factor of this type contributes substantially to the abnormality of *o*-toluic acid. It is thought probable that a hydrogen bond can be formed between an alkyl group and a suitably placed electron-donating atom; Sidgwick and Callow (156) have already postulated chelation in *o*-nitrotoluene (*cf.* Peacock (143) and Evans (55), both of whom have reported similar cases of intramolecular interaction of methyl). Thus the high dissociation constant of *o*-toluic acid may be due to the limited formation of hydrogen bond as shown in formula XV (the explanation offered by Bennett and Mosses (16) refers to an interaction between methyl and carboxyl, but bond formation is not postulated).



On the other hand, an effect of the geometric type may account for the abnormality found in *o*-*tert*-butylbenzoic acid (K/K_u , 5.58; *p*-*tert*-butylbenzoic acid, 0.63 (155)).

In the phenylacetic, β -phenylpropionic, and cinnamic acid systems the carboxyl group is too far removed from the ortho-substituent for bulk influences to intervene, and the positions of the atoms are not suitable for chelation; the absence of ortho-effects in these acids can thus be understood. Inspection of the data for substituted phenylboric acids (appendix) does not reveal an ortho-effect, while in the ortho-substituted phenols any enhancement of strength is not ponderable. This latter feature is attributed to the fact that the charged oxygen of the anion in these cases is weakly electron-donating by comparison with the oxygen of the carboxylate ion.⁴

⁴ Jenkins (J. Chem. Soc. 1939, 1137) has now offered a proof of the non-existence of an ortho-effect in halogeno- and nitro-substituted phenols (and anilines), which goes to show that the inductive effects of the substituents here are very largely responsible for the recorded strengths.

The foregoing views are in harmony with data for the rates of esterification and hydrolysis of ortho-substituted benzoic acids and esters, respectively (see 42, 56). Notably, an ortho-effect is apparent only when the reacting group contains an electron-donating atom.

The case of *o*-methoxybenzoic acid is problematic. Unlike the *p*-isomer, this acid is stronger than the unsubstituted compound; this contrasts also with the behavior of methoxyl in β -phenylpropionic and cinnamic acids. This may be due to the predominance of the inductive effect in the benzoic acid system, where the substituent is situated at such close quarters to carboxyl, meaning that the explanation is an electrostatic one. Very recently, Fox and Martin (62a) have shown, in an infrared spectroscopic investigation, that *p*-methoxybenzoic acid gives the usual carboxylic acid curve, whereas the *o*-methoxybenzoic acid exhibits an additional band of considerable intensity. These authors suggest that the feature may be due to hydrogen-bond formation between OH of carboxyl and the oxygen of methoxyl; it is doubtful, however, whether this would affect the ionization of the acid.

In explanation of the high strengths of *o*-nitro- and *o*-halogeno-benzoic acids it was proposed (42) that oxygen of the carboxylate ion may act as electron-donor in the formation of a coördinate bond with the substituent group. This viewpoint is now rendered unnecessary, however, since Jenkins (102a) (see page 198), by an analysis of the dissociation constants of the isomeric nitro- and halogeno-benzoic acids in the light of classical electrostatic theory and having regard to actual interatomic distances and group moments, has been able to show that these groups behave no less normally when situated in the ortho-position than when placed in the meta- and para-positions, i.e., the large *K* exhibited by the *o*-nitro- and *o*-halogeno-benzoic acids is simply the outcome of induction, probably occurring largely through space. These groups were selected by Jenkins for analysis because they presented the simplest case from the point of view of calculation, but it so happens that they are the only common groups to show always a predominating inductive effect when substituted in organic acids. In all cases they have the effect of increasing *K*, no matter whether substituted in aliphatic or aromatic systems. It can be appreciated, therefore, why data for these acids have been capable of interpretation in electrostatic terms. Mesomeric effects are not accounted for by the theoretical treatment, and where these intervene lack of conformity will be evinced; doubtless this factor is responsible for the displacement of *p*-nitrobenzoic acid.

Calculations involving the methyl and hydroxyl groups would have been more complicated, but in any case the dissociation constant data

present sequences which are not consistent with an explanation based on electrostatic theory alone. This is due to the fact that with these substituents electromeric effects are much more prominent, e. g., hydroxyl is known to cause an increase or decrease in K . Apart from this, there is much more evidence for abnormal behavior of the ortho-substituent in these cases. The effect of methyl in the ortho-position is to increase K , whereas in the meta- and para-positions it reduces K , in accord with normal experience; again, the polar effect of hydroxyl is by no means so different from that of methoxyl as to cause salicylic acid to possess such a vastly superior strength in comparison with *o*-methoxybenzoic acid. Moreover, the explanation offered for the behavior of the methyl and hydroxy acids involves hydrogen-bond formation leading to a six-membered ring with two double bonds, a proposition which contains no novel feature. Indeed, hydrogen-bond formation is regarded as implicit in the suggested resonance of the molecule.

Thus, it now appears that the ortho-effect, with its implication of abnormality, is exhibited in the benzoic acid series only where the ortho-position is occupied either by hydroxyl or methyl substituents or by some particularly bulky group.

Evidence of an ortho-effect in organic acids is not confined to the benzoic acid system. It has already been pointed out (62, 89, 44) that in crotonic acids of *cis*-configuration the substituent group is permanently maintained in a position comparable to that of the ortho-substituent in benzoic acid, and, consequently, a markedly high acid strength is to be anticipated. This is shown below, where it is seen that the *cis*-acids are always much stronger than the *trans*-isomers. The cinnamic acids can be added to this category; allocinnamic acid is about four times as strong as the ordinary (*trans*) acid.

| ACID | $10^5 K$ | ACID | $10^5 K$ |
|------------------------------------|----------|---------------------------------------|----------|
| Crotonic acid..... | 2.03 | Isocrotonic acid..... | 3.6 |
| α -Chlorocrotonic acid..... | 72 | α -Chloroisocrotonic acid..... | 158 |
| Cinnamic acid..... | 3.65 | Allocinnamic acid..... | 13.2 |

The fact that α -naphthoic acid is stronger than β -naphthoic acid doubtless has a similar bearing ($10^5 K = 20.4$ and 6.8 , respectively (18)). This influence is not reflected in the relative strengths of the naphthylboric acids, but analogy is found in the naphthylamines, where the α -isomer is the weaker base.

It scarcely needs to be emphasized that the problem of the ortho-effect is one of great complexity, and other factors, in addition to the influences

which have been discussed, are probably operative. Nevertheless, when a wholly satisfactory explanation of the phenomenon of steric effects is forthcoming, bulk and chelation factors will doubtless prove to be of major significance.

Examination of the classical dissociation constants recorded from time to time for certain 2,3- and 2,5-disubstituted benzoic acids indicates a further factor (quite apart from the ortho-effect) determining the restraint put on the ionization of carboxyl. It is seen that when a meta-substituent is introduced into an ortho-substituted benzoic acid, the effect on K varies according to whether the group is brought into the 3- or the 5-position. In other words, carboxyl is not influenced independently by the two substituents but rather by a resultant effect which is determined, to some

TABLE 11

Comparison of the effects of 3- and of 5-substitution upon the dissociation of an orthosubstituted benzoic acid

| ACID | 10 ³ K | REFER- ENCE | ACID | 10 ³ K | REFER- ENCE |
|-------------------------------|-------------------|----------------|-------------------------------|-------------------|----------------|
| Salicylic acid: | | | <i>o</i> -Chlorobenzoic acid: | | |
| 3-Hydroxy-..... | 1.14 | (140) | 3-Nitro-..... | 8.7 | (90) |
| 5-Hydroxy-..... | 1.08 | | 5-Nitro-..... | 6.2 | |
| 3-Nitro-..... | 15.7 | (140) | <i>o</i> -Nitrobenzoic acid: | | |
| 5-Nitro-..... | 8.9 | | 3-Chloro-..... | 4.4 | (90) |
| <i>o</i> -Chlorobenzoic acid: | | | 5-Chloro-..... | 14.2 | |
| 3-Hydroxy-..... | 1.4 | (33) | 3-Nitro-..... | 14.4 | (157) |
| 5-Hydroxy-..... | 1.4 | | 5-Nitro-..... | 26.4 | |

extent, by the influence which these groups exert upon each other. From the data in table 11 it is seen that with *o*-nitrobenzoic acid a greater enhancement of strength is brought about by introduction of the meta-substituent into the 5-position, whereas with salicylic and *o*-chlorobenzoic acids greater strength is associated with substitution in the 3-position, although there are cases where the differences are negligible.

H. The saturated aliphatic acids

Reliable data are now available for the strengths of the normal series of fatty acids extending from acetic to nonoic acid, together with those of certain analogs. These results are considered separately, because their discussion involves, to some extent, arguments embodied in the interpretation of the ortho-effect.

In the first place, the normal acids, excluding *n*-butyric acid, are found to fall in strength as the series is ascended, and the decrease is most pronounced in passing from acetic to propionic acid. Such behavior is in harmony with our knowledge of the inductive effects ($+I$) of alkyl groups; the sequence of strengths is conveniently represented in figure 3 (for the complete list of constants see the appendix). This compares with the findings of Evans, Gordon, and Watson (57), who studied the alkaline hydrolysis of the ethyl esters of these normal acids; on ascending the series the energy of activation gradually rises, as anticipated in a class B reaction (i.e., one which is facilitated by withdrawal of electrons from the seat of reaction) when the $+I$ effect of the substituent group increases.

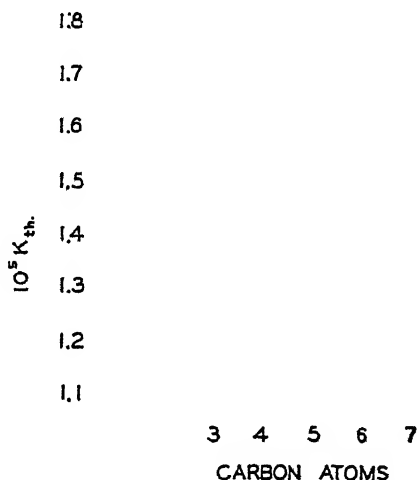
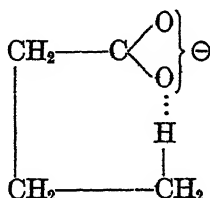


FIG. 3. Plot of the number of carbon atoms in the alkyl chain against values of $10^5 K^+_{th}$. 1, acetic acid; 2, propionic acid; 3, *n*-butyric acid; 4, *n*-valeric acid; 5, *n*-hexoic acid; 6, *n*-heptoic acid; 7, *n*-octoic acid; 8, *n*-nonoic acid.

It is evident that *n*-butyric acid behaves anomalously, for its dissociation constant is definitely high. Attention has already been drawn to this by Bennett and Mosses (16), who point out that the terminal methyl group of *n*-butyric acid compares in its situation with the methyl group of *o*-toluic acid, and they postulate, consequently, that the abnormalities exhibited by these acids have a common origin: namely, an interaction of methyl and carboxyl in space. They also state that the abnormality is less marked in the fatty acid because the approach of methyl to the carboxyl group is intermittent here, on account of free rotation of the chain. The conception of hydrogen-bond formation as applied to *o*-toluic acid may supply an interpretation of this spatial interaction in the case of

n-butyric acid; thus high acid strength would be attributed to the reluctance of hydrion to recombine with the anion in consequence of the following process (41):



Evidence of another kind also shows that the ionization of *n*-butyric acid is affected by some disturbance. Harned and Sutherland (86) record for this acid a value of $\theta = 8^\circ\text{C}$. (temperature of maximum *K*), whereas with other acids of this order of strength θ lies between 20° and 25°C .

From the data ($10^5 K$) tabulated below (41) it is seen that the dissociation constants of isobutyric and diethylacetic acids are also relatively high; this is to be expected, since these acids also possess the three-carbon alkyl chain. Moreover, the chain branching leads to more frequent approach of the terminal methyl groups to carboxyl, and this would account for the sequence



which is the converse of the order that would arise from operation of inductive effects alone.

| | | | | | |
|----------------------------|-------------------|--------------------|------|-------------------------|-------------------|
| Acetic acid..... | 1.75 ₈ | | | | |
| Propionic acid.... | 1.33 ₈ | Isobutyric acid.. | 1.38 | Trimethylacetic acid... | 0.891 |
| <i>n</i> -Butyric acid.... | 1.50 | Isovaleric acid... | 1.67 | Diethylacetic acid..... | 1.77 ₈ |
| <i>n</i> -Valeric acid.... | 1.38 | | | | |

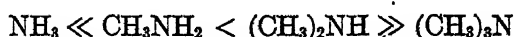
Inspection of figure 3 shows that *K* for propionic acid is somewhat low by comparison with the succeeding normal acids, and it seems that if all the points representing the higher normal acids were displaced downwards with respect to propionic acid, a perfectly continuous sequence from acetic acid would be revealed. This is probably due to those acids above *n*-butyric acid being involved also, to some extent, in a chelation process. It is a necessary outcome of the view already expressed that hydrogen of γ -methylene should always be capable of forming a bond along the lines suggested. The influence of a chelation factor cannot be traced in the data for unsaturated aliphatic acids, owing, no doubt, to its being masked by the preponderating additional polar effects introduced by the ethenyl grouping.

Chain branching at the α -carbon atom leads to acid strengths which

reveal an entirely different problem. From the preceding table it is seen that substitution of a single methyl group in propionic acid at the α -carbon atom does not bring about a fall in K , although with introduction of two methyl groups there is a very appreciable diminution; it is significant that with other acids of the type XCH_2COOH (where X is a substituent other than alkyl) a proportionate fall in K is observed when one methyl group substitutes in the α -position (41).

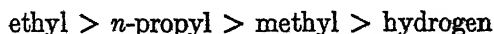
There is a striking analogy between the relative strengths of *p*-ethyl-, *p*-isopropyl-, and *p*-*tert*-butyl-benzoic acids (10^5K : 4.43, 4.43, and 3.98, respectively) and of propionic, isobutyric, and trimethylacetic acids (10^5K : 1.33, 1.38, and 0.891, respectively); moreover, it seems as though their interpretations must be identical. The aromatic acids differ from the aliphatic acids only in that a benzene nucleus separates carboxyl from the alkyl group, so that influences arising in the latter will be transmitted readily in both systems. It appears that the partial inversion of the polar effects of ethyl, isopropyl, and *tert*-butyl encountered in the alkyl-benzoic acids is being observed once again, and the alternative suggestions due to Baker and Nathan (9) and to the present writer (39, 41) should provide an explanation.

The order of the energies of activation for the alkaline hydrolysis of acetic, propionic, isobutyric, and triethylacetic acids (57) indicates a similar feature (it should be noted that a group which causes a diminution of K in an acid brings about an increase in the energy of activation in a class B reaction). Again, the strengths of the methylamines present the order



It seems that here an increasing restraint is being put on the inductive effect of methyl as methylation of ammonia proceeds, and this compares with the conclusions drawn above in the case of acids.

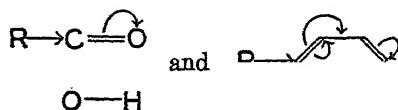
It is also interesting to note the changes brought about in basic strengths upon lengthening the alkyl chain. The results of Hall and Sprinkle (75) for the *N*-alkyl- and *N,N*-dialkyl-anilines indicate throughout that the ionization is facilitated not in the manner anticipated from operation of the normal inductive effects but always in the order



meaning that either the ethyl or *n*-propyl group is behaving anomalously.

Finally, formic acid, the first member of the fatty acid series, presents a peculiar problem. It is distinct from its homologs in that its dissociation constant is greater by a power of ten; in other words, introduction of alkyl into formic acid brings about a change of surprising magnitude. It should

be kept in mind, however, that introduction of methyl into benzene brings about a striking increase of reactivity in substitution reactions, and there is an analogy between the two processes (cf. 98).



I. Sundry substituents

Our knowledge of the influences of other groups upon dissociation constants is not by any means so adequate. Nevertheless, where evidence is forthcoming, it is in harmony with observations regarding the effects of these groups upon other processes.

The acetyl group in aromatic substitution is known to be strongly meta-orienting, and consequently the group is electron-attracting. This would follow from the fact that acetyl, containing carbonyl, presents a positively charged carbon at its point of attachment. Thus, it is to be anticipated that the strength of pyruvic acid will be relatively high ($K = 3.2 \times 10^{-3}$ (21); cf. acetic acid, $K = 1.76 \times 10^{-5}$). The enhancing influence of acetyl is only slight, however, when it replaces hydrogen in the hydroxyl group of *m*- and *p*-hydroxybenzoic acids, and the order of strengths

m-acetoxybenzoic acid > benzoic acid > *p*-acetoxybenzoic acid

is preserved, which means that oxygen attached directly to the nucleus is the predominant factor here.

| | K/K_u | |
|--------------------------------|------------|------------|
| | <i>m</i> - | <i>p</i> - |
| Acetoxybenzoic acid (140)..... | 1.58 | 0.67 |
| Hydroxybenzoic acid (23)..... | 1.32 | 0.46 |

Again, the cyano group presents an example of a well-defined electron-attractive substituent (K/K_u for cyanoacetic acid, 205 (140)). Its influence is known to be similar to that of the nitroxyl group, e.g., the dipole moments (*D*) of *p*-tolyl cyanide and nitrobenzene are 4.37 and 4.42, respectively (in benzene solution at 22°C.) (161), and this is also reflected in the following comparison of acid strengths: K/K_u for *p*-cyanobenzoic acid, 4.9 (162); for *p*-nitrobenzoic acid, 6.0 (43).

The influence of the nitrosyl substituent is also noteworthy. It has been shown by Ingold (95) that substitution of nitrosobenzene leads to the

para-derivative, and Robinson (145) states that this is to be anticipated. Hammick and Illingworth (82), however, claim that this result is a consequence of the complexity of the reacting molecule under the prevailing conditions, and that when the compound is in unimolecular condition the nitroso group is meta-directing. Introduction of this substituent into an aliphatic acid certainly increases the strength greatly (K/K_u for α -nitroso-propionic acid, 37 (164)), and this is in keeping with the depression of basic strength found in passing from dimethylaniline to *p*-nitrosodimethylaniline (see appendix).

It is convenient to include in this category of miscellaneous acids the few measurements made very recently on certain organic deuterio-acids in deuterium oxide as solvent.

Lewis and Schutz (120), employing the minute cell devised by Lewis and Doody (119), have determined conductimetrically the strengths (10^5K) of CH_3COOD and CH_2ClCOOD (0.59 and 63, respectively). As stated by these workers, the differences in zero point energy indicate that proton is bound in the hydro-acid less firmly than deuteron in the deuterio-acid, and consequently deuterio-acids should be the weaker, as is found to be the case (cf. acetic acid, 1.76; chloroacetic acid, 137.8). Moreover, it was also pointed out that the weaker the acid (i.e., the stronger the bond) the greater the relative difference between the strengths of hydro- and deuterio-acids (compare Halpern (76)). This is borne out by the foregoing data and by the ratios ($K_{\text{D}_2\text{O}}/K_{\text{H}_2\text{O}}$) for oxalic, formic, and acetic acids recorded by Schwarzenbach, Epprecht, and Erlenmeyer (153) (cf. Hornel and Butler (92)).

V. THE QUANTITATIVE CORRELATION OF DISSOCIATION CONSTANTS

A certain amount of attention has been devoted to the numerical correlation of dissociation constants with other physical characteristics, notably dipole moments, and a summary of the attempts in this direction is given here.

On the grounds that the free energy of ionization of an acid can be expressed as $RT \log K$, Derick (37) suggested, several years ago, that the relative polar effects (negativity or positivity) of the radicals in organic acids are best represented quantitatively as $-1000/\log K$ (the negative sign is convenient), and, consequently, the influence of a substituent is given by the ratio

$$\frac{1000}{\log K} / \frac{1000}{\log K_u}$$

where K is the dissociation constant of the substituted acid and K_u that of the parent unsubstituted acid. Later Waters (166), also taking the view

that the change in free energy of ionization is a measure of the influence of the substituent, endeavored to show that the values of $\log K$ for certain substituted benzoic acids ($\text{XC}_6\text{H}_4\text{COOH}$) were linear functions of the dipole moments (μ , in Debye units) of the corresponding substituted benzenes (XC_6H_5) (a quantity which also expresses the polarity of the molecule). Actually, the strengths of the meta-substituted acids were examined, for here complicating factors such as tautomeric and steric effects were considered to be absent. Indeed, it is reasonable to assume that a quantitative connection between K and μ will exist when the polar influences determining their magnitude are comparable, i.e., when only permanent or "polarization" effects operate in the molecule. Waters' relationship, however, proved to be only very approximate.

The connection between dissociation constant and dipole moment has also been emphasized by Smallwood (158), who has endeavored to show by calculation that the change in the K for an acid, brought about by introduction of a substituent, is determined largely by the magnitude and orientation of the moments of the substituents. From a knowledge of group moments and molecular dimensions, he has estimated values for the changes in energy of ionization, and these agree with experimental figures deduced from actual dissociation constant data (compare the new development due to Kirkwood and Westheimer (111a) connecting K and the electrostatic influence of the substituent group; by means of this mathematical formulation Westheimer and Shookhoff (170a) have accounted for the ratios of the dissociation constants of a few monobasic acids).

A little later, Nathan and Watson (132) succeeded in demonstrating that for the common substituted acetic acids the plot of $\log K$ against μ (in Debye units) is a curve of the form

$$\log K = \log K_u - x(\mu + a\mu^2)$$

where x and a are constants for the series. When sufficient accurate data (K_{th}) for substituted benzoic and phenylacetic acids became available, it was found (47, 48) that the points for the meta-substituted acids were situated on a similar curve, although x and a differed from series to series, e.g., for benzoic acids $x = 0.402$ and $a = 0.14$; for phenylacetic acids $x = 0.125$ and $a = 0.076$. The values of dipole moments employed were those for benzene solutions at a fixed temperature; more satisfactory values, relating to vapors, have since been forthcoming, but on replotting very similar results have been obtained (169).

Upon examination of the elementary possibility that K (for benzoic and phenylacetic acids) is itself very simply related to μ (for mono-substituted benzenes (71, 124)), it was found by the author (38, 46) that the points for the meta-substituted acids are collinear (although where methyl is the sub-

stituent the para-substituted acids are included; see below). In figure 4 the points for the phenylacetic acids are plotted; consideration of the methoxy compounds is now excluded, because doubt exists as to the "effective" moment of the methoxyl substituent, which is an inclined group. The relationship has been extended to the β -phenylpropionic series (still employing the dipole moments of mono-substituted benzenes), although it has been shown that with cinnamic acids the points are somewhat irregular; it is appreciated that in the latter series the existence of a double bond in the side chain considerably affects the polarity of the molecule, and thus a comparison with the substituted benzenes is rendered unsound.

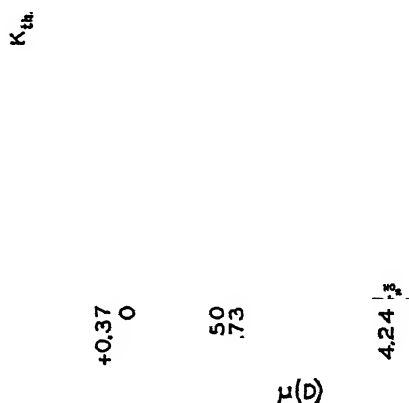


FIG. 4. Plot of μ (in Debye units) for mono-substituted benzenes against values of $10^5 K_{th}$ for substituted phenylacetic acids.

It has already been mentioned that in the case of the methyl substituent the para-substituted acids, and not the meta-substituted acids, are included in these relationships. This indicates that in toluene the permanent electromeric displacements make a very substantial contribution to the measured moment, in contrast to halogeno- and nitro-benzenes, where apparently the moments are largely the outcome of the intrinsic electron-attractive capacities of the substituents (cf. 9). In other words, a considerable part of the polar effect of methyl, as measured in μ for toluene, is inoperative from the meta-position as, for example, in *m*-toluic and

m-tolylacetic acids (169). In the phenylacetic acid series the points representing the halogeno-substituted acids are on the line (figure 4), showing that any abnormality due to the mesomeric influence has become comparatively insignificant. Again, it would be seen that the points for the *p*-halogeno acids fall well below the line, and that for the *p*-nitro acid, above the line; these divergences are due to the different extents to which electromeric displacements occur in the acids and substituted benzenes. Any connection which this linear relationship may have with the earlier equation proposed by Nathan and Watson is not obvious. It may be that the linear equation, within the narrow limits of its application (it has been applied in each case to acids the strengths of which vary by little more than an order of ten), is simply an approximation of a broader relationship. It certainly has the advantage of being exacting and simple to apply and, at the same time, involves no arbitrary constants.

A different type of correlation has been attempted by Hammett (81, 77), who connects the logarithms of the dissociation constants of acids (or bases) with the velocity constant data for reactions of compounds related in constitution to the acids (or bases), e.g., the strengths of benzoic acids are connected in this way with alcoholysis rates of benzoyl chlorides. In a number of such cases Hammett and other workers (29, 36, 36a, 144a, 88a, 26a) have demonstrated approximate linearity; moreover, similar results have been obtained when $\log K$ for two related series of acids or $\log k$ for two series of comparable reactions are plotted (80), although it appears that in aliphatic systems the scope of the relationship is limited. The success of these studies has led Hammett (79) to propose a simple formula to represent the influence of a meta- or para-substituent upon the velocity or equilibrium constant of a reaction in which the reacting group is in the side chain; after an analysis of data for a large number of reactions, a table of "reaction" and "substituent" constants was compiled (the effect of a substituent in any given reaction is the product of the appropriate constants).

The equation of Nathan and Watson, cited earlier, has been shown to apply just as well to velocity coefficient data as to dissociation constants (K is simply replaced by k) (132,133,58). In view of this Dippy and Watson (48) have combined the equations,

$$\log K = \log K_u - x(\mu + a\mu^2)$$

$$\log k = \log k_u - y(\mu + b\mu^2)$$

and show that a linear relationship between $\log K$ and $\log k$ is indicated only if $a = b$. Calculations show that there is no such equality in the coefficients of the μ^2 term, although they may be of the same order of magnitude. Thus Hammett's relationship is not an outcome of known

expressions involving μ . Certain of the results discussed by Hammett and by Burkhardt (29) have been replotted by Dippy and Watson with the aid of more reliable dissociation constant data, but distinct divergences still occur; these are inevitable when strict proportionality does not exist between electromeric effects, and this applies especially to the para-substituted systems included in the relationship.

From time to time efforts have been made to estimate the effect upon dissociation constants brought about by removing the substituent along a chain. In 1902 Wegscheider (170) stated that K for a substituted acid was the product of K for the unsubstituted acid and a factor determined by the position of the substituent; he deduced a table of such factors. Again, Derick (37) claimed, as a result of his calculations, that the dissociation constants of α -, β -, γ -, and δ -substituted aliphatic acids were related to the dissociation constants of the unsubstituted acids by a "rule of thirds", although this applied only where powerful electron-attractive groups were involved.

The relationship of MacInnes (125) is particularly interesting; here the dissociation constants of hydroxy- and halogeno-aliphatic acids are connected with the distance of the substituent along the carbon chain. Straight lines were obtained on plotting $\log K$ against $1/d$, where $d = 1, 2, 3$, etc. for α -, β -, γ -(etc.)substitution, meaning that the data fit the equation

$$\log K = C + S \frac{1}{d}$$

(C and S are constants which depend on the nature of the substituent.) The assumption is made that the constant C is the logarithmic function of the dissociation constant of the hypothetical acid obtained by moving the substituent an infinite distance along a chain, although, as MacInnes points out, this K must not be identified with the K of an unsubstituted long-chain acid. It has been claimed that this formula also holds reasonably well for methyl-, hydroxy-, and halogeno-benzoic acids, if the relative distances (d) separating carboxyl and the substituent in the ortho-, meta-, and para-positions are taken to be 1, $\sqrt{3}$, and 2, respectively, i.e., the distances across a regular hexagon. The applicability of the formula has since been extended, although largely in connection with aliphatic amino compounds (54, 68, 152). Recently Greenstein (69) has given this relationship a more precise physical significance; he replaces d by l , where l is the distance, in Ångström units, between the dipole center of the group and the carboxyl center (assuming an extended chain); the molecular dimensions recorded by Pauling were employed in calculating l .

The success of the MacInnes relationship is certainly striking, as far as

it applies to saturated aliphatic systems. Where the inductive effect of the substituent alone operates, it should follow, as a consequence of the definition of this effect, that the magnitude of the dissociation constant of an acid will be governed in a simple manner by the distance separating carboxyl and the substituent group. It is noteworthy, however, that in the benzoic acid series the MacInnes equation fails to hold good when the present trustworthy dissociation constants data are plotted; this is to be expected in a system where tautomeric effects operate (from the ortho-

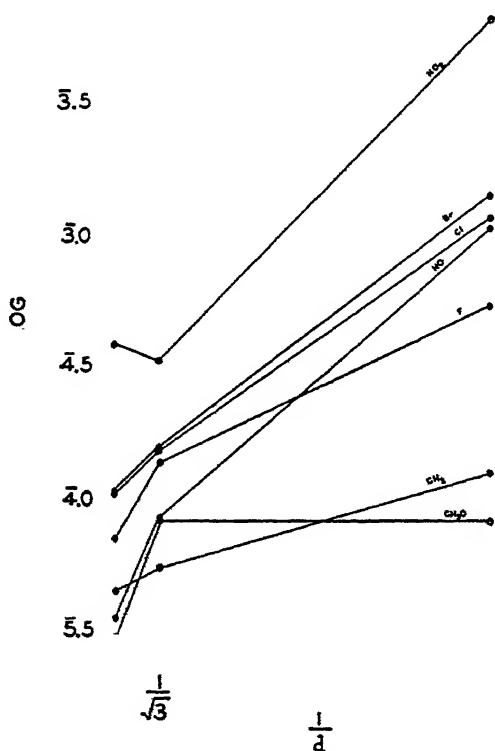


FIG. 5. Plot of $1/d$ against $\log K$ for various substituted benzoic acids

and para-positions) in addition to the inductive effects, and where steric influences may introduce complications. From figure 5 it is seen that serious irregularities occur with the hydroxy-, methoxy-, and fluoro-benzoic acids, as well as with the nitrobenzoic acids (mentioned by MacInnes), and these cannot be corrected by making allowance for the suggested "puckering" of the ring.

Very recently, Jenkins (102a) reëxamined the connection between acid strength and the distance separating carboxyl and the substituent group. He has succeeded in finding a linear relation between $\log K$ (for *o*-, *m*-, and

p-isomers) and the electric intensity due to the substituent dipole (calculated from a knowledge of dipole moment and interatomic distances) in the case of nitro- and halogeno-benzoic acids. This relation has an important bearing on views expressed in regard to the ortho-effect in acids (discussed on page 186), although its applicability is bound to be limited.

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APPENDIX

The scope of this review is limited to monobasic acids. The dissociation constants assembled in the following tables have been determined by modern methods of procedure. Strengths of phenols and bases that are relevant to the discussion are included for the sake of completeness. Data are expressed as thermodynamic constants (K_{th}) except those obtained by Hall and Sprinkle and W. C. Davies, who prefer to record their results for bases in terms of pK_H .

Several independent measurements of K_{th} have been made on certain of the acids, and agreement, on the whole, is good. The bulk of the data

refer to aqueous solution, although in some investigations aqueous alcoholic solutions have been employed. The standard temperature throughout is 25°C., except where otherwise stated. Where several values of K are given for one acid, the first one is the one cited in the discussions of this paper.

I. ACIDS

(1) Saturated aliphatic carboxylic acids

| ACID | VALUES OF $10^5 K$ IN AQUEOUS SOLUTION | METHOD USED* | EXPERIMENTERS |
|-----------------------------|--|--------------|-----------------------------------|
| Formic acid..... | 17.12 | E | Harned <i>et al.</i> (83, 84, 86) |
| Acetic acid..... | 1.75 ₅ | C | Dippy (41) |
| | 1.754 | E | Harned <i>et al.</i> (83, 84, 86) |
| | cf. 1.753 | C | MacInnes and Shedlovsky (126) |
| | 1.759 | C | Ives, Linstead, and Riley (99) |
| | 1.764 | C | Jeffery, Vogel, and Lowry (102) |
| Propionic acid..... | 1.33 ₅ | E | Harned <i>et al.</i> (83, 84, 86) |
| | cf. 1.343 | C | Belcher (12a) |
| <i>n</i> -Butyric acid..... | 1.50 | C | Dippy (41) |
| | cf. 1.515 | E | Harned <i>et al.</i> (83, 84, 86) |
| | 1.508 | C | Belcher (12a) |
| Isobutyric acid..... | 1.38 | C | Dippy (41) |
| <i>n</i> -Valeric acid..... | 1.38 | C | |
| Isovaleric acid..... | 1.67 | C | |
| <i>n</i> -Hexoic acid..... | 1.32 | C | |
| <i>n</i> -Heptoic acid..... | 1.28 | C | |
| <i>n</i> -Octoic acid..... | 1.27 ₅ | C | |
| <i>n</i> -Nonoic acid..... | 1.11 | C | |
| Trimethylacetic acid..... | 0.891 | C | |
| Diethylacetic acid..... | 1.77 ₅ | C | |
| Chloroacetic acid..... | 137.8 | E | Wright (175) |

* C = conductimetric method; E = Harned's cell method.

(2) *Unsaturated aliphatic carboxylic acids*

| ACID | VALUES OF $10^5 K$ IN AQUEOUS SOLUTION | METHOD USED* | EXPERIMENTERS |
|--|--|--------------|---------------------------------|
| Acrylic acid..... | 5.56 | C | Dippy and Lewis (44) |
| <i>cf.</i> 5.501 | | C | German, Jeffery, and Vogel (64) |
| <i>trans</i> -Crotonic acid..... | 2.03 | C | Ives, Linstead, and Riley (99) |
| <i>cf.</i> { 2.030 | | C | German, Jeffery, and Vogel (64) |
| | 1.97 _s | C | Saxton and Waters (151) |
| Vinylacetic acid..... | 4.48 | C | Ives, Linstead, and Riley (99) |
| <i>cf.</i> 4.62 | | C | Dippy and Lewis (44) |
| Δ^{α} - <i>n</i> -Pentenoic acid..... | 2.02 | C | |
| Δ^{β} - <i>n</i> -Pentenoic acid..... | 3.11 | C | Ives, Linstead, and Riley (99) |
| Δ^{γ} - <i>n</i> -Pentenoic (allylacetic) acid..... | 2.10 | C | |
| <i>cf.</i> 2.11 _s | | C | Dippy and Lewis (44) |
| β,β -Dimethylacrylic acid..... | 0.76 | C | Ives, Linstead, and Riley (99) |
| <i>cf.</i> 0.7569 | | C | German, Jeffery, and Vogel (64) |
| Δ^{α} - <i>n</i> -Hexenoic acid..... | 1.98 | C | |
| Δ^{β} - <i>n</i> -Hexenoic acid..... | 3.05 | C | |
| Δ^{γ} - <i>n</i> -Hexenoic acid..... | 1.91 | C | |
| Δ^{δ} - <i>n</i> -Hexenoic acid..... | 1.90 | C | |
| γ -Methyl- Δ^{α} -pentenoic acid... | 1.99 | C | |
| γ -Methyl- Δ^{β} -pentenoic acid.... | 2.51 | C | Ives, Linstead, and Riley (99) |
| <i>trans</i> - β -Methyl- Δ^{α} -pentenoic acid..... | 0.74 | C | |
| <i>cis</i> - β -Methyl- Δ^{α} -pentenoic acid..... | 0.71 | C | |
| δ -Methyl- Δ^{γ} -hexenoic acid.... | 1.59 | C | |
| Tetrollic acid..... | 222.8 | C | German, Jeffery, and Vogel (64) |

conductimetric method.

(3) *Aromatic carboxylic acids*(a) *Values of 10^5K for acids of the benzoic acid series in aqueous solution* 10^5K for benzoic acid = 6.27^a; cf. 6.527^b, 6.373^c, 6.295^d, 6.312^e

| POSITION OF SUBSTITUENT | CH ₃ | C ₂ H ₅ | iso-C ₄ H ₉ | tert-C ₄ H ₉ | C ₆ H ₅ | CH ₃ O | C ₆ H ₅ O | HO |
|-------------------------|--------------------------------|---|-----------------------------------|------------------------------------|-------------------------------|---------------------------------------|--|---------------------------------------|
| <i>o</i> - | 12.3 ₅ ^a | | | | 34.7 ^a | 8.06 ^a (8.2 ^f) | 29.7 ^a | 105 ^g (107 ^h) |
| <i>m</i> - | 5.35 ^a | | | | | 8.17 ^a (9.0 ^f) | 11.2 ^a | 8.3 ^g (8.71 ^h) |
| <i>p</i> - | 4.24 ^a | 4.43 ₅ ^a | 4.43 ^a | 3.98 ^a | | 3.38 ^a (3.6 ^f) | 3.00 ^a | 2.9 ^g (3.31 ^h) |
| | F | Cl | | Br | I | NO ₂ | | |
| <i>o</i> - | 54.1 ^a | 114 ^a (119.7 ^h) | | 140 ^a | 137 ^a | 671 ^a | 10^5K for 2-methyl-6-nitrobenzoic acid = 1335 ^a | |
| <i>m</i> - | 13.6 ₅ ^a | 14.8 ^a (15.06 ^h) | | 15.4 ^a | 14.1 ^a | 32.1 ^a | | |
| <i>p</i> - | 7.22 ^a | 10.5 ₅ ^a (10.4 ^h) | | 10.7 ^a | | 37.6 ^a | | |

^a Dippy and coworkers (51, 52, 43, 45, 8, 46); conductimetric method.^b Ives, Linstead, and Riley (99); conductimetric method.^c Vogel and Jeffery (163); conductimetric method.^d Saxton and Meier (150); conductimetric method.^e Brockman and Kilpatrick (27); conductimetric method.^f Branch and Yabroff (23); potentiometric method.^g Kuhn and Wassermann (114); potentiometric method.(b) *Values of 10^5K for acids of the benzoic acid series in 50 per cent aqueous methyl alcohol solution^a* 10^5K for benzoic acid = 0.513

| POSITION OF SUBSTITUENT | F | Cl | Br | I |
|-------------------------|-------|------|-------|------|
| <i>o</i> - | 6.61 | 7.08 | 7.08 | 6.6 |
| <i>m</i> - | 1.41 | 1.45 | 1.35 | 1.41 |
| <i>p</i> - | 0.832 | 1.00 | 0.933 | 1.00 |

^a Kuhn and Wassermann (114); potentiometric method at 17–20°C.(c) *Values of 10^5K for acids of the benzoic acid series in 25 per cent aqueous ethyl alcohol solution^a* 10^5K for benzoic acid = 2.29

| POSITION OF SUBSTITUENT | HO | CH ₃ O |
|-------------------------|-------|-------------------|
| <i>o</i> - | 63.8 | 2.09 |
| <i>m</i> - | 2.43 | 2.87 |
| <i>p</i> - | 0.750 | 1.16 |

^a Branch and Yabroff (23); potentiometric method.

(d) Values of 10^5K for acids of the phenylacetic acid series in aqueous solution 10^5K for phenylacetic acid = 4.88^a; cf. 4.88^b

| POSITION OF SUBSTITUENT | CH ₃ | C ₂ H ₅ | iso-C ₂ H ₅ | tert-C ₄ H ₉ | CH ₂ O | F | Cl | Br | I | NO ₂ |
|-------------------------|-------------------|-------------------------------|-----------------------------------|------------------------------------|-------------------|-------------------|-------------------|-------------------|-------------------|-------------------|
| <i>o</i> - | | | | | | | 8.60 ^a | 8.84 ^a | 9.16 ^a | 9.90 ^a |
| <i>m</i> - | | | | | | | 7.24 ^a | | 6.93 ^a | 10.8 ^a |
| <i>p</i> - | 4.27 ^a | 4.24 ^a | 4.06 ^a | 3.82 ^a | 4.36 ^a | 5.68 ^a | 6.45 ^a | 6.49 ^a | 6.64 ^a | 14.1 ^a |

| ACID | 10^5K |
|-------------------------------------|-------------------|
| 3,4-Dimethoxyphenylacetic acid..... | 4.64 ^a |
| Mandelic acid..... | 38.8 ^c |
| 2,4-Dinitrophenylacetic acid..... | 31.5 ^a |

^a Dippy and coworkers (50, 51, 43, 45); conductimetric method.^b Jeffery and Vogel (101); conductimetric method.^c Banks and Davies (12); conductimetric method.(e) Values of 10^5K for acids of the β -phenylpropionic acid series in aqueous solution^a 10^5K for β -phenylpropionic acid = 2.19

| POSITION OF SUBSTITUENT | CH ₃ | CH ₂ O | Cl | NO ₂ |
|-------------------------|-------------------|-------------------|------|-------------------|
| <i>o</i> - | 2.17 | 1.57 | 2.65 | 3.13 ₅ |
| <i>m</i> - | 2.10 ₅ | 2.22 | 2.60 | |
| <i>p</i> - | 2.07 | 2.04 ₅ | 2.47 | 3.36 |

^a Dippy and coworkers (44, 46); conductimetric method.(f) Values of 10^5K for acids of the cinnamic acid series^a in aqueous solution^a 10^5K for *trans*-cinnamic acid = 3.65; for *cis*-cinnamic acid = 13.2

| POSITION OF SUBSTITUENT | CH ₃ | HO | CH ₂ O | Cl | NO ₂ |
|-------------------------|-------------------|-------------------|-------------------|-------------------|-----------------|
| <i>o</i> - | 3.16 ₅ | 2.44 | 3.45 | 5.83 | 7.07 |
| <i>m</i> - | 3.61 ₅ | 4.00 ₅ | 4.21 | 5.08 ₅ | 7.58 |
| <i>p</i> - | 2.73 | | 2.89 | 3.86 | 8.99 |

^a Dippy and coworkers (44, 45, 46); conductimetric method.^{*} All of the acids given in the table are *trans*-modifications.(g) Values of 10^5K for some unclassified acids in aqueous solution^a

| ACID | 10^5K |
|-----------------------------------|---------|
| Diphenylacetic acid..... | 11.5 |
| γ -Phenylbutyric acid..... | 1.75 |
| Cinnamylideneacetic acid..... | 3.75 |

^a Dippy and coworkers (50, 44); conductimetric method.

(4) Phenylboric acids

(a) Values of $10^{10}K$ for monosubstituted phenylboric acids* in 25 per cent aqueous ethyl alcohol^a $10^{10}K$ for phenylboric acid = 1.97; 13.7†; 0.164‡

| POSITION OF SUBSTITUENT | CH ₃ | C ₆ H ₅ | C ₂ H ₅ O | C ₆ H ₅ O | F | Cl | Br | NO ₂ |
|-------------------------|-----------------|-------------------------------|---------------------------------|---------------------------------|------|------|------|-----------------|
| <i>o</i> - | 0.261 (1.81†) | (0.00984†) | 0.910 | | | 14.0 | | 5.6 |
| <i>m</i> - | 1.4 | (0.185†) | 3.05 | | 11.0 | 13.5 | 14.6 | 69 |
| <i>p</i> - | 1.0 | (0.158†) | 0.068 | 0.116 | 3.66 | 6.30 | 7.26 | 98 |

| OTHER BORIC ACIDS | | $10^{10}K$ |
|--------------------------------|--|-----------------|
| Boric acid..... | | 1.34 (6.53†) |
| Unclassified boric acids: | | |
| β-Phenylethylboric acid..... | | 1.81 (1.0†) |
| <i>n</i> -Butylboric acid..... | | 0.0344 (0.182†) |
| Benzylboric acid..... | | 1.49 (7.55†) |
| α-Naphthylboric acid..... | | 0.888 |
| β-Naphthylboric acid..... | | 2.6 |

* Branch, Yabroff, *et al.* (178, 24, 179, 19); potentiometric method.* RB(OH)₂ is, in effect, a monobasic acid, since K appears to be constant over a range of concentrations.

† In water.

‡ In 50 per cent aqueous ethyl alcohol.

(5) Phenols

(a) Values of $10^{10}K$ for monosubstituted phenols $10^{10}K$ for phenol = 0.32^a; 0.123^b

| POSITION OF SUBSTITUENT | F a | Cl | | | Br a | I a |
|-------------------------|--------|------|------|------|---------|--------|
| | | a | b | c | | |
| <i>o</i> - | 4.27 | 10.2 | 3.2 | 7.97 | 9.78 | 9.12 |
| <i>m</i> - | 1.51 | 4.90 | 1.95 | 3.30 | 4.37 | 3.89 |
| <i>p</i> - | 0.76 | 1.32 | 0.47 | 1.46 | 1.55 | 2.19 |

* Bennett, Brooks, and Glasstone (14); 30 per cent aqueous ethyl alcohol solution; potentiometric method.

^b Kuhn and Wassermann (114); 50 per cent aqueous methyl alcohol solution; temperature, 20°C.; potentiometric method.

* Branch, Yabroff, and Bettmann (24); 25 per cent aqueous ethyl alcohol solution; potentiometric method.

II. BASES

(a) Values of $10^5 K_B$ for methylamines in aqueous solution^a

| BASE | $10^5 K_B$ |
|---------------------|------------|
| Methylamine..... | 43.8 |
| Dimethylamine..... | 52.0 |
| Trimethylamine..... | 5.45 |
| Ammonia..... | 1.79 |

^a Harned and Owen (85); Harned's alternative cell method.(b) Values of $10^{12} K_B$ for monosubstituted anilines in 80 per cent aqueous ethyl alcohol^a
 $10^{12} K_B$ for aniline = 126

| POSITION OF SUBSTITUENT | F | Cl | Br | I |
|----------------------------|--------------|------|------|------|
| <i>o</i> - | 2.95 (9.20*) | 1.35 | 1.00 | 0.36 |
| <i>m</i> - | 10.5 (25.7*) | 8.51 | 7.94 | 7.59 |
| <i>p</i> - | 120 (441*) | 28.8 | 21.9 | 15.1 |

^a Bennett, Brooks, and Glasstone (14); potentiometric method.

* In aqueous solution.

(c) Values of $10^5 K_B$ for monosubstituted benzylamines in aqueous solution^a
 $10^5 K_B$ for benzylamine = 2.35

| POSITION OF SUBSTITUENT | CH ₃ | CH ₂ O | |
|----------------------------|-----------------|-------------------------------|---|
| <i>o</i> - | 1.70 | 5.56 | |
| <i>m</i> - | 2.40 | 1.56 | |
| <i>p</i> - | 2.55 | 3.22 | |
| | CH ₃ | C ₂ H ₅ | <i>iso</i> -C ₂ H ₇ |
| <i>N</i> -alkyl | 3.80 | 4.75 | 4.18 |

^a Carothers, Bickford, and Hurwitz (30); potentiometric method.(d) Values of $10^5 K_B$ for other phenylamines in aqueous solution^a

| AMINE | $10^5 K$ |
|--|----------|
| β -Phenylethylamine..... | 6.78 |
| γ -Phenylbutylamine..... | 24.8 |
| δ -Phenylpropylamine..... | 15.9 |
| ϵ -Phenylamylamine..... | 30.6 |
| β -Phenylethylmethylaniline..... | 13.9 |

^a Carothers, Bickford, and Hurwitz (30); potentiometric method.

In the last four tables (e, f, g, and h) given in the appendix, the results obtained by Hall and Sprinkle (75) and by Davies and coworkers (36, 36a) are presented. These authors give their results in terms of pK_H . These constants are more easily calculated and involve no assumption of the value of K_w . The values follow the same trend as the K_B data.

(e) Values of pK_H for amines of the aniline series^a in aqueous solution
 pK_H for aniline = 4.62

| POSITION OF SUBSTITUENT | CH ₃ | CH ₃ O | C ₂ H ₅ O |
|----------------------------|-----------------|-------------------|---------------------------------|
| <i>o</i> - | 4.39 | 4.49 | 4.47 |
| <i>m</i> - | 4.69 | 4.20 | 4.17 |
| <i>p</i> - | 5.12 | 5.29 | 5.25 |

| N-ALKYL DERIVATIVES | pK_H | N-ALKYL DERIVATIVES | pK_H |
|---|--------|--|--------|
| <i>N</i> -CH ₃ | 4.85 | <i>N</i> -CH ₃ , <i>N</i> - <i>n</i> -C ₃ H ₇ | 5.64 |
| <i>N</i> -C ₂ H ₅ | 5.11 | <i>N</i> , <i>N</i> -(C ₂ H ₅) ₂ | 6.56 |
| <i>N</i> - <i>n</i> -C ₃ H ₇ | 5.02 | <i>N</i> -C ₂ H ₅ , <i>N</i> - <i>n</i> -C ₃ H ₇ | 6.34 |
| <i>N</i> , <i>N</i> -(CH ₃) ₂ | 5.06 | <i>N</i> , <i>N</i> -(<i>n</i> -C ₃ H ₇) ₂ | 5.59 |
| <i>N</i> -CH ₃ , <i>N</i> -C ₂ H ₅ | 5.98 | | |

^a Hall and Sprinkle (75); potentiometric method.

(f) Values of pK_H for unclassified amines in aqueous solution^a

| | pK_H |
|--------------------------|--------|
| Ammonia..... | 9.27 |
| Diphenylamine... | 0.85 |
| Triphenylamine... | 0 |
| Cyclohexylamine.. | 10.61 |
| α -Naphthylamine. | 3.92 |
| β -Naphthylamine. | 4.11 |
| 2-Aminodiphenyl.. | 3.78 |
| 4-Aminodiphenyl.. | 4.27 |
| Pyridine..... | 5.21 |
| Piperidine..... | 11.13 |

^a Hall and Sprinkle (75); potentiometric method.

(g) Values of pK_H for derivatives of dimethylaniline in 30 per cent aqueous ethyl alcohol at 20°C.*

pK_H for dimethylaniline = 4.76

| POSITION OF SUBSTITUENT | CH ₃ | CH ₃ O | C ₂ H ₅ O |
|-------------------------|-----------------|-------------------|---------------------------------|
| <i>o</i> - | 5.42 | | |
| <i>m</i> - | 4.86 | | |
| <i>p</i> - | 5.29 | 5.53 | 5.59 |

* Davies and coworkers (36, 36a); potentiometric method.

(h) Values of pK_H for derivatives of dimethylaniline in 50 per cent aqueous ethyl alcohol at 20°C.*

pK_H for dimethylaniline = 4.21

| POSITION OF SUBSTITUENT | CH ₃ | C ₂ H ₅ | C ₃ H ₇ | <i>iso</i> -C ₃ H ₇ | <i>n</i> -C ₄ H ₉ | <i>tert</i> -C ₄ H ₉ | CH ₃ O | F | Cl | Br | I | NO |
|-------------------------|-----------------|-------------------------------|-------------------------------|---|---|--|-------------------|------|------|------|------|------|
| <i>o</i> - | 5.07 | | | | | | 5.49 | | | | | |
| <i>p</i> - | 4.77 | 4.69 | 4.43 | 4.78 | 4.62 | 4.65 | 5.16 | 4.01 | 3.33 | 2.82 | 2.73 | 3.52 |

pK_H for diethylaniline = 5.85; for di-*n*-butylaniline = 4.84

* Davies and coworkers (36, 36a); potentiometric method.

THE CHEMISTRY OF AMINOGUANIDINE AND RELATED SUBSTANCES

EUGENE LIEBER AND G. B. L. SMITH

Department of Chemistry, Polytechnic Institute of Brooklyn, Brooklyn, New York

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I. INTRODUCTION

Aminoguanidine and its derivatives have been the subjects for many important, interesting, and fruitful investigations. The researches on these substances, extending over a period of about fifty years, have occupied the time and energies of a great many chemists in several countries. Thiele was the first to prepare aminoguanidine in 1892, and contributions to our knowledge of the compound have been made by Pellizzari, Hantzsch, Curtius, and other renowned chemists. Aminoguanidine and the many closely related substances have such remarkable properties that Richter in his treatise on organic chemistry uses the term "*merkwürdig*" in reference to them. In fact, many of the first compounds of certain classes have been derived from aminoguanidine as a parent substance, and the studies on aminoguanidine have contributed much to our knowledge of heterocyclic compounds, the higher hydronitrogens, the guanazyls, the azides, and nitron. Despite these facts, the importance and significance of the compound in the organic chemistry of nitrogen have been missed by many scholars.

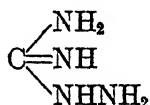
Although much important and interesting work has been carried out on aminoguanidine and related compounds, no review of the results achieved has previously been made. The lack of appreciation of the fundamental character of the work may be attributed to this fact. The papers on these subjects are rather widely scattered in the literature. Accordingly, the authors have undertaken to present a review of the chemistry of aminoguanidine and related compounds. It is their hope that the presentation will serve as a stimulus and guide to further work in the field, as many of the excellent studies are still incomplete in certain phases. Hence, one of their aims is to point out some of these gaps in our knowledge and to invite their completion. The authors believe, also, that a knowledge of aminoguanidine and related compounds is essential to a complete understanding of the organic chemistry of nitrogen. For this reason they sincerely hope that the review will be of interest to the general reader.

II. SYNTHESIS OF AMINOGUANIDINE

Several methods for the formation and preparation of aminoguanidine have been developed. These methods may be classified in three categories, as follows: (A) reduction, (B) hydrazination, and (C) hydrazinolysis.¹

A. Reduction of nitro- and nitroso-guanidines

Thiele (147) was the first to prepare aminoguanidine and to suggest its probable constitution:



He obtained the compound by the reduction of nitroguanidine (24, 132, 136) with zinc dust in a solution of acetic acid (7). A modified form of his procedure has been described recently by Conard and Shriner (20). In a later paper Thiele (151) described the preparation and properties of aminoguanidinium bicarbonate and established its constitution from analytical data. The bicarbonate, owing to its insolubility, is the most convenient compound to use for recovering aminoguanidine from solution, especially when the solution contains guanidine, because this substance does not form an insoluble carbonate or bicarbonate.

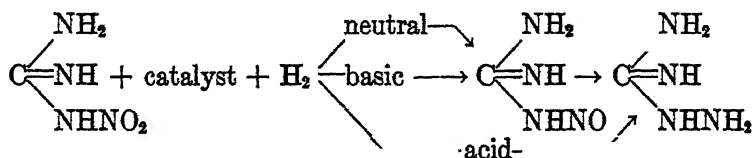
Wyler (179), in 1935 and 1938, obtained patents for the preparation of aminoguanidine by the reduction of nitroguanidine at 40°–50°C. with zinc as a reducing agent in the presence of an aqueous solution of zinc or another metal acetate. Fuller, Lieber, and Smith (51) reduced nitroguanidine in liquid ammonia solution with metallic sodium, and were able to prepare aminoguanidine in 60 per cent yield provided the reduction was carried out in the presence of a sufficient concentration of ammonium chloride. The optimum stoichiometrical ratios of sodium : ammonium chloride : nitroguanidine were 6:6:1. With smaller quantities of ammonium chloride only reddish brown products of unknown composition were obtained, and in the absence of ammonium chloride cyanamide was the only compound identified among the reduction products.

Boehringer (10), in 1903, claimed to have obtained aminoguanidine in yields as high as 80 per cent by the electrolytic reduction of nitroguanidine suspended in a dilute solution of sulfuric acid; he employed a tin cathode, a current density of 250 amperes per square meter, and a temperature of

¹ Hydrazination is a reaction in which hydrazine is added, and the term is analogous to hydration. Hydrazinolysis is a metathetical reaction with hydrazine, and the term is analogous to hydrolysis.

10°C. Workers at the Polytechnic Institute of Brooklyn have as yet failed to confirm this observation.

McGill (83) has recently suggested that aminoguanidine may be manufactured by the hydrogenation of nitroguanidine with a catalyst of nickel dispersed on kieselguhr at temperatures between 25° and 125°C. and in the *absence* of any substantial amounts of acid. A more comprehensive examination of the catalytic hydrogenation of nitroguanidine has been made by Lieber and Smith (78). Contrary to the results of McGill (83), it was found that the optimum conversion to aminoguanidine is obtained in media of relatively high acid concentration. The molar ratio of hydrogen to hydrogen acceptor obtained in the catalytic hydrogenation of nitroguanidine was found to depend upon the experimental conditions and may be summarized as follows:



In acid of such a concentration that the molar ratio of nitroguanidine to acid is 1 or higher, the reduction proceeds without the formation of nitrosoguanidine. In neutral and basic media, nitrosoguanidine is the first product of reduction and can be readily isolated in good yield. Lieber and Smith (81) have recently employed catalytic hydrogenation in the reduction of α -alkyl- γ -nitroguanidines.

Thiele (149) found that the action of zinc dust upon nitrosoguanidine dissolved in a solution of acetic acid yielded aminoguanidine, but he did not record quantitative details. Lieber and Smith (79) have studied, quantitatively, the catalytic hydrogenation of nitrosoguanidine to aminoguanidine, and have found that nitrosoguanidine is more resistant to reduction by this method than is nitroguanidine.

Thiele (147) prepared and analyzed aminoguanidinium chloride, hexachloroplatinate, nitrate, sulfate, and picrate. He also described a complex salt of copper, a beautiful violet-blue substance, and gave its formula as $(\text{CN}_4\text{H}_5)_2\text{Cu}(\text{HNO}_3)_2$, but from our present knowledge we would consider it a substituted hydrazino complex and write the formula $[(\text{CN}_4\text{H}_5)_2\text{Cu}](\text{NO}_3)_2$. G. S. Smith (130) has prepared the analogous coordination complex of nickel and has interpreted his data in a like manner. The aminoguanidinium phosphotungstate (145), tetrabromoaurate (57), hexabromotellurite (56), and tetrachloropalladate (55) have been described, and in addition a complex compound with thiourea (5) has been prepared.

Hantzsch (58) has shown that a primary sulfate of aminoguanidine is formed in absolute sulfuric acid, aminoguanidine in this case acts as a tetraacid base. The formula of the salt may be written as $[\text{CN}_4\text{H}_{10}] \cdot (\text{HSO}_4)_4$.

Aminoguanidine may be regarded as a derivative of hydrazine (*vide infra*) and it forms an especially interesting series of salts, two representatives of which are described by Thiele (147). The salts have already been referred to and are the aminoguanidinium bicarbonate and bisulfate. Kertesz (unpublished notes) in this laboratory has prepared aminoguanidinium dinitrate, and Lieber (unpublished notes) has obtained the aminoguanidinium dichloride. It is, therefore, evident that aminoguanidine in these compounds possesses the property, analogous to hydrazine, of *functioning as a diacid base*. In other words, these compounds are secondary rather than primary salts.

Suida (145) has found that with acid dyes aminoguanidine forms compounds which are sparingly soluble in water. Ekeley and Swisher (35) studied the action of aminoguanidinium bicarbonate on the addition products of benzalanilines and sodium bisulfite. The reaction between molecular quantities of benzalaniline and sodium bisulfite in aqueous solution gives an unstable product which decomposes when separated from the mother solution. The aqueous solution of such a product reacts with 1 mole of aminoguanidinium bicarbonate, and primary anilino-benzylaminoguanidinium sulfite,



is immediately precipitated.

G. S. Smith (129) has described a volumetric procedure for the determination of aminoguanidine, which is essentially an adaptation of the early Jamieson (72) method for hydrazine. The aminoguanidinium salt (approximately 0.1 g.) dissolved in 50 ml. of water is treated with 20 ml. of 5 *N* sulfuric acid and 50 ml. of 0.1 *N* potassium iodide; the solution is allowed to stand for 3 min. in a glass-stoppered flask; an excess of potassium iodide is added and the liberated iodine is titrated immediately with a standard solution of sodium thiosulfate.²

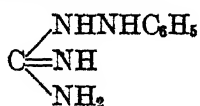
² In some recent studies in this laboratory Thomas G. Wheat has found that the hydrazino nitrogen in the semicarbazones of a number of aldehydes and ketones may be estimated by the Jameson technique of titration with a standard solution of potassium iodate. (See Thomas G. Wheat: Thesis, B.S. in Chemistry, Polytechnic Institute of Brooklyn, June, 1938; also G. B. L. Smith and T. G. Wheat: Ind. Eng. Chem., Anal. Ed. 11, 200 (1939).)

B. Hydrazination

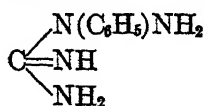
1. Cyanamide and its derivatives

Pelizzari and Gaiter (102), in 1914, improved their earlier method (101) for the preparation of aminoguanidine from cyanamide and hydrazine sulfate. Prior to this work Hofmann and Ehrhart (64) had used calcium cyanamide and hydrazine sulfate. Fantl and Silbermann (37) have recently improved this general procedure so that they obtain 90 to 95 per cent yields of aminoguanidine, starting from crude disodium cyanamide.

The preparation of a mono-substituted aminoguanidine was first recorded by Pellizzari (94). By the reaction of phenylhydrazine hydrochloride on cyanamide, in alcoholic solution, a substance was obtained which he termed "anilino-guanidine." In a more careful study of the reaction Pellizzari (95) showed that only 50 per cent of the expected anilguanine is obtained and that an isomer, amidophenylguanidine (phenylhydrazonocarbamidine or *as*-phenylguanylhiazine), is also formed:



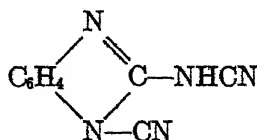
Anilguanine



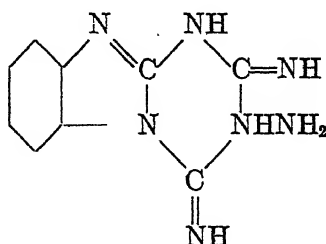
"Amidophenylguanidine"

"Amidophenylguanidine" was readily separated from its isomer by condensation with aldehydes. By using phenylhydrazinium bromide Pellizzari (96) effected a more direct separation, since the amidophenylguanidininium bromide was found to be more soluble in water and less soluble in alcohol than its isomer was. Pellizzari and Tivoli (106) attempted to prepare anilguanine in pure form by the reaction of cyanogen chloride with phenylhydrazine. In this study anilcyanamide, $\text{C}_6\text{H}_5\text{NHNHCN}$, was first formed, and while its reaction with water gave phenylsemicarbazide, the corresponding reaction with ammonia did not take place. Instead, polymerization occurred and a substance which was believed to be dianil-dicyandiamide, $(\text{C}_6\text{H}_5\text{NHNHCN})_2$, was formed. Pellizzari and Cuneo (101) showed that the reaction of cyanamide with hydrazines was a general one, and prepared a number of α -(arylamino)guanidines. A more recent application of this reaction is described by Fantl and Silbermann (37).

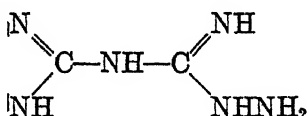
In 1921 Pellizzari (97) studied the reaction of cyanogen chloride with phenylhydrazine in aqueous solution and showed that the initial product of the reaction is *o*-phenylene- α , β -dicyanguanidine,



This substance on further reaction with hydrazine hydrate gave 3-amino-1,2,3,4-tetrahydro-2,4-diiminotriazinobenzimidazole (*o*-phenyleneamino-isomelamine).

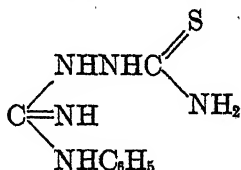


The action of alkali converts the 4-imino group to a carbonyl group. The resulting melanuric acid is unstable and loses carbon dioxide; the ring is ruptured and benzimidazoleaminoguanidine (*o*-phenyleneaminobiguanide) is formed:



o-Phenyleneaminobiguanide

Arndt and Tschenschner (4) have shown that the reaction of phenylcyanamide with thiosemicarbazide forms thiocarbamidophenylaminoguanidine (α -phenyl- γ -thioureidoguanidine):



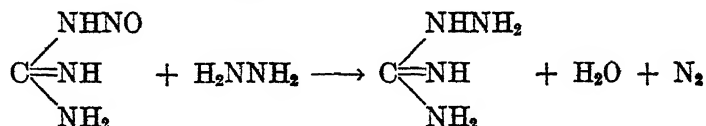
2. Dicyandiamide

The reaction of hydrazine hydrate with dicyandiamide was studied by Stollé and Krauch (143). These investigators isolated aminoguanidine, diaminoguanidine, triaminoguanidine, and aminobiguanide from the reaction mixture, besides a number of interesting nitrogen heterocyclic derivatives, which will be considered later. These former substances are no doubt the precursors of the nitrogen ring compounds.

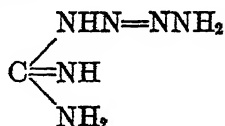
C. Hydrazinolysis

1. Nitrosoguanidine

Thiele (149), in 1893, discovered that equimolecular proportions of nitrosoguanidine (125) and hydrazine hydrate react readily, with evolution of nitrogen, to form aminoguanidine:



The intermediate, a tetrazene,



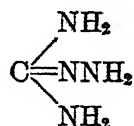
was considered to form, and immediately lose nitrogen. However, when the reaction was conducted with the ratio of 2 moles of nitrosoguanidine to 1 mole of hydrazine hydrate, a much slower reaction took place, and the product was hydrazodicarbamidine:



The first substance formed is aminoguanidine, as indicated above. This in turn reacts with additional nitrosoguanidine to form the tetrazene



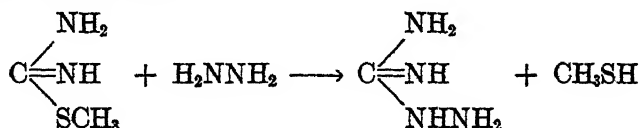
in which loss of nitrogen results in the formation of hydrazodicarbamidine. Thiele considered that this was proof that aminoguanidine did not have the "symmetrical" form:



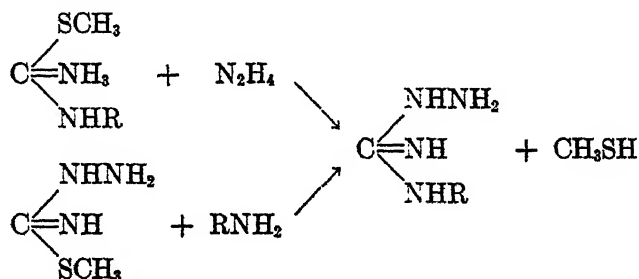
Thiele (149) suggested as an alternative mechanism for the formation of hydrazodicarbamidine that the nitrosoguanidine first "dearranged" (25, 26) to water, nitrogen, and cyanamide; that cyanamide combined with the hydrazine to form aminoguanidine; and that this compound in turn reacted with a second mole of cyanamide to form hydrazodicarbamidine. About the same time, Pellizzari (101) found that the reaction of cyanamide and hydrazine hydrochloride led to the formation of aminoguanidine.

2. Thiourea and its derivatives

Heyn (63), in 1926, received a patent on a method for the preparation of aminoguanidine and substituted aminoguanidines based on the reaction of hydrazine or substituted hydrazines with *S*-alkylisothiurea sulfates. Aminoguanidinium sulfate was prepared from hydrazine hydrate and methylisothiurea sulfate:

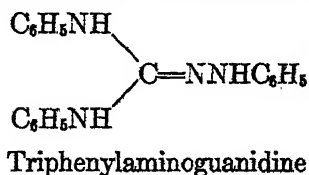


Substantially the same process was patented by Schering-Kahlbaum (126) two years later. Smith and Anzelmi (131) have confirmed the observation of Heyn (63); they obtained aminoguanidinium sulfate in quantitative yield. Kirsten and Smith (73) have prepared α -alkyl- γ -aminoguanidines by this general method and have employed the two following general schemes of synthesis:

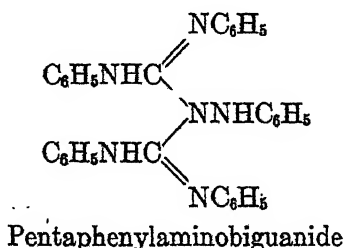


Busch and Bauer (16) have found that the reaction between hydrazine and thiourea in the presence of lead oxide or mercuric oxide does not give aminoguanidine; this reaction is prevented apparently by the oxidation of the hydrazine by the metallic oxides. However, these authors found that the reaction could be carried out in an alcoholic solution of potassium hydroxide, and they prepared a number of α, β -diaryl- γ -aminoguanidines from the respective diarylthiourea and hydrazine hydrate. These substances were found to be very strong bases, and they formed well-crystallized salts. If the reaction is carried out in the absence of alcoholic potassium hydroxide, only arylthiosemicarbazides are formed (18).

In 1888¹ Marchwald (86) prepared triphenylaminoguanidine



("diphenylanilguanidine" or α, γ -diphenyl- β -(anilino)guanidine) by the action of lead oxide on an alcoholic solution of thiocarbamide and phenylhydrazine. A little later, Marchwald and Wolff (87) prepared the same substance by the action of lead oxide with an alcoholic solution of diphenylthiosemicarbazide and aniline. Wessel (172) attempted to prepare the material by the reaction of carbodiphenylimide ($\text{C}_6\text{H}_5\text{N}=\text{C}=\text{NC}_6\text{H}_5$) with phenylhydrazine, but obtained a substance having a melting point of 204°C ., whereas the compound of Marchwald and Wolff (87) melted at 160°C . Pyrolysis of triphenylaminoguanidine at elevated temperatures led to the formation of ammonia, benzene, phenylhydrazine, and a white substance believed to be identical with Wessel's (172) product, since it melted at 201°C . Its composition, $\text{C}_{32}\text{H}_{28}\text{N}_6$, was believed to correspond to a pentaphenylaminobiguanide:



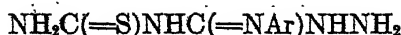
3. Dithiureas and thiocarbonates

A concentrated solution of hydrazine hydrate reacts with arylthiobiurets and yields an arylthiurea and thiosemicarbazide. However, Arndt (3) and Fromm, Bruck, Runkel, and Mayer (45) found that if dilute hydrazine hydrate solutions are used, hydrogen sulfide is liberated and two isomeric (aminoguanyl)arylthiureas are formed



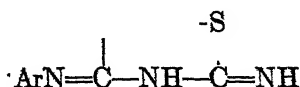
I

and

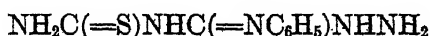


II

I is basic and II acidic in nature. II appears to be the chief product of the reaction. Of the two isomers only I can be isolated readily in the form of well-defined salts. Thiurets (47)



are the basic oxidation products of the arylthiobiurets discussed above. Fromm, Kayser, Briegleb, and Fohrenbach (48) studied the reaction of hydrazine with phenylthiuret and found that the initial reaction led to the formation of two isomeric (aminoguanyl) derivatives:



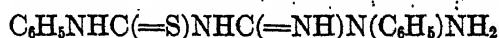
III

and



IV

The (aminoguanyl)phenylthiourea (IV) appears to be the main product. Fromm and Vetter (49) and Fromm and Weller (50) studied the corresponding reaction with phenylhydrazine. Of the four isomers theoretically possible, it was shown that only two, V and VI, are formed:



V

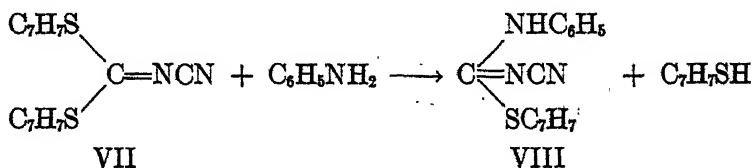
and



VI

Phenyl(aminoguanyl)phenylthiourea (V) was isolated (49) from the reaction mixture in crystalline form. Weller (50) prepared phenyl(aminoguanyl)*p*-tolylthiourea by the reaction of phenylhydrazine on *p*-tolylthiuret.

Hantzsch and Wolvekamp (60) found that persulfocyanic acid reacts with benzyl chloride in the presence of potassium hydroxide and forms dibenzylcyanamidodithiocarbonate (VII). Subsequently, Fromm and Goncz (46) found that VII reacts with aniline to form α -phenyl- γ -benzyl- β -cyanoisothiurea (VIII):

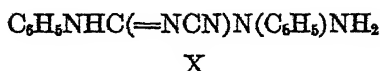


This substance reacts with phenylhydrazine, and two isomeric cyano(aminoguanido) derivatives (IX and X) are formed,



IX

and

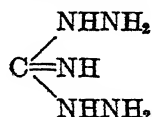


III. SYNTHESSES OF CLOSELY RELATED COMPOUNDS

Diaminoguanidine and triaminoguanidine are closely related to aminoguanidine in properties and reactions, but they have not been so extensively studied. They are prepared by methods which involve both hydrazination and hydrazinolysis. Diaminoguanidine has also been prepared by the reduction of nitroaminoguanidine, and, only comparatively recently, by the hydrazination of the "dearrangement" products of nitroguanidine.

A. Diaminoguanidine

There are apparently only three general methods for the preparation of diaminoguanidine (α, γ -diaminoguanidine):

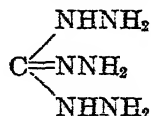


Diaminoguanidine

Stollé (139), Stollé and Hofmann (142), Pellizzari and Cantoni (100), and Pellizzari and Roncagliolo (105) prepared diaminoguanidinium chloride or bromide by allowing equimolecular proportions of cyanogen chloride or bromide to react with hydrazine in ethereal or aqueous solutions. The method was improved by Pellizzari and Gaiter (102). The isolation of diaminoguanidine from the reaction product of hydrazine hydrate and dicyandiamide (143) has been mentioned. The third method of preparation is the reduction of nitroaminoguanidine with zinc dust in a solution of acetic acid (107).

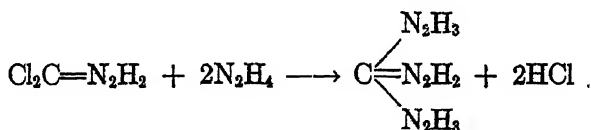
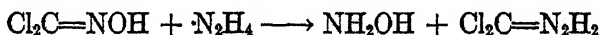
B. Triaminoguanidine

Stollé (138) first prepared triaminoguanidine



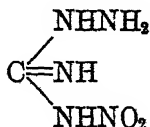
Triaminoguanidine

by the action of hydrazine hydrate on carbon tetrachloride at its boiling point and later (143) isolated the substance from the reaction products of hydrazine hydrate and dicyandiamide. Pellizzari and Gaiter (102) found that diaminoguanidine, aminoguanidine, or guanidine reacting with 1, 2, or 3 moles of hydrazine hydrate, respectively, gave triaminoguanidine. The reaction took place with ease in water or alcohol on heating from 2 to 5 hr. Schotte (128), in 1926, obtained a patent on the preparation of triaminoguanidine and its derivatives by treating isothioureia ethers with an excess of hydrazine or its derivatives. Prandtl and Dollfus (113) found that in aqueous solution dichloroformoxime, $\text{Cl}_2\text{C}=\text{NOH}$, is reduced by hydrazine to hydrocyanic acid. However, if an ethereal solution of dichloroformoxime is added, while cooling, to an ether emulsion of hydrazine hydrate, triaminoguanidine is readily formed. They explained its formation by the intermediate decomposition of dichloroformoxime to chloroformyl-nitrile oxide (chlorine isocyanate), $\text{ClC}\equiv\text{NO}$, which is subsequently converted to cyanogen chloride. In the presence of excess hydrazine, this forms triaminoguanidine. An alternative and more reasonable mechanism, which was suggested by one of the reviewers of this paper, may be formulated as follows:



C. Nitroaminoguanidine

Phillips and Williams (107) found that hydrazine sulfate reacts with nitroguanidine to form nitroaminoguanidine



Nitroaminoguanidine

and gave as proof of its structure the reduction to the known derivative diaminoguanidine, as well as its ability to form derivatives with aldehydes and ketones (133, 173). The ultraviolet absorption of aqueous solutions of nitroaminoguanidine has recently been examined (119).

IV. REACTIONS OF AMINOGUANIDINE

The properties and reactions of aminoguanidine are profoundly different from those of guanidine. In fact, many of the properties of this substance are more nearly like those of hydrazine than those of guanidine, and aminoguanidine may be regarded as a substituted hydrazine,—guanylh-dydrazine. On the other hand, the guanyl group modifies the properties of hydrazine, especially in regard to basic properties, since aminoguanidine is a stronger base than hydrazine. We have no information in regard to the dearrangement of the compound. The mechanisms of some of the simpler conversions and transformations of aminoguanidine have not been definitely established.

The products of the reactions of aminoguanidine and some of its derivatives with carbonyl compounds have been studied rather extensively. Nitroaminoguanidine is potentially of importance in organic analysis as a reagent for the identification of aldehydes and ketones. Aminoguanidine and its other derivatives have not been investigated from this point of view, but some of these compounds should prove useful.

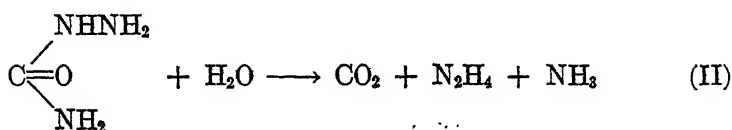
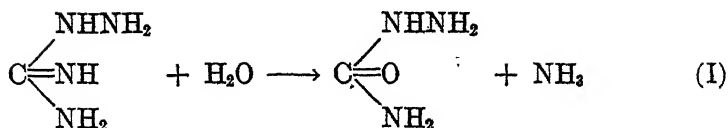
The hydrolytic reactions of aminoguanidine are of interest, but our knowledge of these reactions, particularly the reactions of the "free base," is quite fragmentary. Much the same situation exists in regard to the oxidation reactions of aminoguanidine. No physicochemical studies are recorded concerning reactions of these two types.³

Nitrous acid reacts with aminoguanidine, and the products formed are of great interest to workers in nitrogen chemistry. It has taken fully a quarter of a century to establish the structures of these products, and a number of investigators have contributed to these studies. We have attempted to systematize the known facts regarding the reactions of aminoguanidine with nitrous acid under different conditions.

A. Hydrolytic reactions

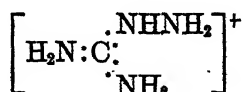
Thiele (147) found that the hydrolysis of aminoguanidine proceeds in two stages: semicarbazide is formed in the first stage, and further hydrolysis yields hydrazine, ammonia, and carbon dioxide. The presence of semicarbazide was established by the preparation of benzaldehyde semicarbazone. This compound was identical with the product formed from the reaction of benzaldehyde, potassium cyanate, and hydrazine (23). The hydrolytic reaction of aminoguanidine may be formulated as follows:

³ Charles Hahn, working in this laboratory, has measured the oxidation potential of the nitrosoaminoguanidine system. The system is reversible in both the acid and the alkaline region. These results will be published in the near future (see Charles Hahn: Thesis, M.S. in Chemistry, Polytechnic Institute of Brooklyn, June, 1938).

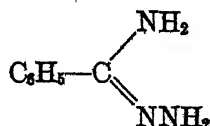


The intermediate semicarbazide was obtained in large quantities when the hydrolysis was effected with sodium carbonate instead of sodium hydroxide.

Lieber and Smith (80) have studied, quantitatively, the hydrolysis of aminoguanidine in acid and basic media. They found that, contrary to the opinions expressed in the literature (83), aminoguanidine is extremely resistant to acid hydrolysis. In dilute solutions of strong mineral acid aminoguanidine and semicarbazide were found to be resistant to hydrolysis, but in solutions of higher concentrations semicarbazide was nearly completely hydrolyzed in times and under conditions such that aminoguanidine was only slightly hydrolyzed. This is probably attributable to the strong basic properties of aminoguanidine in contrast to the weak basic properties of semicarbazide. Also, the aminoguanidinium ion probably has the following structure:⁴

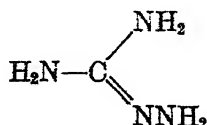


Thiele (147) attempted to prepare free aminoguanidine by precipitation of barium sulfate from a solution of aminoguanidinium sulfate with the stoichiometrical quantity of barium hydroxide. He found that the solution so obtained gradually turned reddish in the air, and, when evaporated *in vacuo*, left behind a red, crystalline material having basic properties. He did not analyze the material. In 1897 Pinner (109) found that an excess of hydrazine reacted with benzimido esters and yielded 3,6-diphenyl-1,2-dihydrotetrazine. He assumed that the following substance

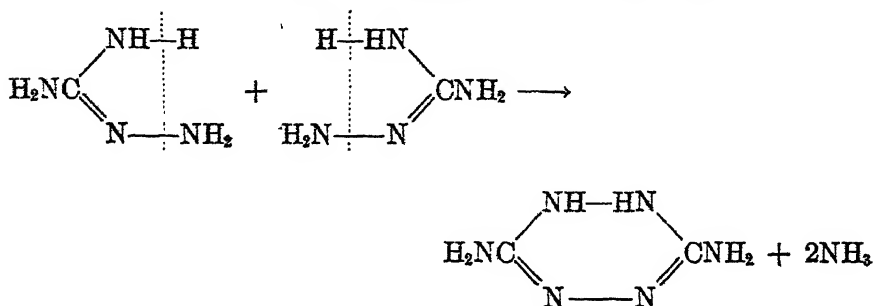


⁴ See also Davis, Yelland, and Ma: J. Am. Chem. Soc. 59, 1993 (1937).

was its precursor. Ponzio and Gastaldi (110), in 1913, reasoning from the facts found by Pinner, argued that aminoguanidine, since it could also assume the form



should therefore be expected to undergo the following reaction:



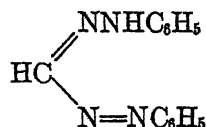
and form 3,6-diamino-1,2-dihydropyrimidine. They found that if the substance was formed, it was immediately oxidized to *s*-diaminotetrazine:



A solution of aminoguanidinium chloride, when treated with a stoichiometrical amount of a solution of potassium hydroxide and evaporated slowly over concentrated sulfuric acid, yielded reddish violet prisms with a metallic luster. This product was slightly soluble in water and gave an intense red-violet solution, from which the original product could be recrystallized if a small amount of ammonia was present. This material is fairly stable in alkaline solution, but on boiling ammonia is evolved. In acidic solutions it forms reddish orange solutions which are decolorized by heating, and on prolonged boiling nitrogen, ammonia, carbon dioxide, and hydrazine are formed. Orange crystalline salts of this material are formed. In later work Ponzio and Gastaldi (111) established the structure of *s*-diaminotetrazine through a study of its reduction products.

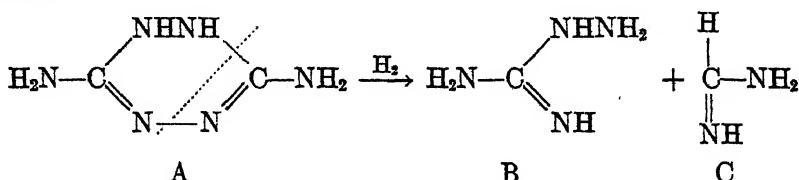
When *s*-diaminotetrazine was suspended in water and treated with hydrogen sulfide, it dissolved and sulfur was precipitated. The presence of aminoguanidine in the solution was established by its isolation as

benzaldehyde guanyldiazide. Phenylhydrazine reduced *s*-diaminotetrazine in an alcoholic solution of acetic acid, and, when gas evolution ceased, diphenylformazyl hydride

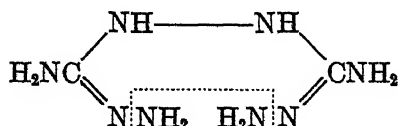


Diphenylformazyl hydride

was isolated. The mechanism of this reduction may be formulated as follows:



Continued reduction of A yields B, and the unstable ammonioformic acid (C) is hydrolyzed, giving formic acid and ammonia. The formic acid reacts with phenylhydrazine, and formylphenylhydrazine, $\text{C}_6\text{H}_5\text{NHNHCHO}$, is formed. This compound in turn reacts with the excess of phenylhydrazine and yields $\text{C}_6\text{H}_5\text{NHNHCH}=\text{NNHC}_6\text{H}_5$, the phenylhydrazone of formylphenylhydrazine. This substance is readily oxidized to the "formazyl" derivatives. In 1915 Ponzio and Gastaldi (112) were able to show that *s*-diaminotetrazine is obtained by the mild pyrolysis of aminoguanidinium bicarbonate. This probably accounts for the variation of the melting point of aminoguanidinium bicarbonate with the rate of heating, as found by Thiele (151). Ponzio and Gastaldi (110) suggested the following mechanism for the formation of *s*-diaminotetrazine: a small quantity of aminoguanidine decomposes to form hydrazine. Subsequently the hydrazine combines with aminoguanidine to form "hydrazinodicarbohydrazine."



The substance undergoes ring closure, through loss of hydrazine, to form *s*-diaminotetrazine.

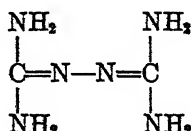
The hydrolysis of diaminoguanidine and of triaminoguanidine does not appear to have been studied. Gaiter (52) found that *s*-tetrabenzoyldiaminoguanidine on hydrolysis yields *s*-dibenzoylhydrazine and ammonia.

B. Oxidation reactions

Thiele (147) oxidized aminoguanidinium nitrate in dilute nitric acid with a solution of potassium permanganate and obtained a yellow basic substance of the composition $C_2H_6N_6$. This material was isolated as the nitrate. On hydrolysis with water, this nitrate yielded ammonium nitrate and an orange-yellow neutral compound, $C_2H_4N_4O_2$. On reduction $C_2H_4N_4O_2$ was converted to a colorless, neutral compound of the composition $C_2H_6N_4O_2$. This latter substance was $H_2NCONHNHCONH_2$, hydrazodicarbamide, since it was identical with the product obtained from the reaction of 2 moles of potassium cyanate with hydrazine sulfate. The base $C_2H_6N_6$ on reduction gave another base, $C_2H_8N_6$, and Thiele (147) therefore assigned the following structure to the oxidation product, $C_2H_6N_6$,



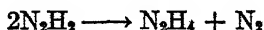
and called it "azodicarbamide." Thiele (147) argued that if aminoguanidine possessed the symmetrical structure, then a base of the composition $C_2H_6N_6$ could not be formed, but would have the following composition and structure:



Thiele argued, also, that azodicarbamide could not be formed from the guanidine, possibly resulting from the oxidation of aminoguanidine, because guanidine was not oxidized under conditions which readily led to the oxidation of aminoguanidine. Hydrolysis of azodicarbamide in the presence of hydrochloric acid yields carbon dioxide, nitrogen, and hydrazodicarbamide. This latter substance is also obtained by the reduction of azodicarbamide, as stated previously. Thiele believed that the hydrolysis of azodicarbamide resulted in the formation of ammonia, carbon dioxide, and diimide. Diimide in turn reduced azodicarbamide to hydrazodicarbamide and was itself oxidized to nitrogen.



Thiele (148) attempted to isolate diimide, but was able to obtain only hydrazine and nitrogen. He believed that diimide reacted with itself as follows:



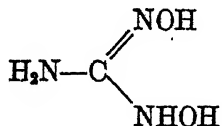
No systematic investigation of the oxidation of aminoguanidine has been recorded.

Triphenylaminoguanidine turns to a red color on standing in air. Marchwald and Wolff (87) have shown this to be due to the formation of an azo derivative:



They isolated this substance as red needles with a metallic luster by oxidation of triphenylaminoguanidine with mercuric oxide. Hence triphenylaminoguanidine probably only exists in the unsymmetrical form as indicated by the formation of the azo derivative by oxidation. A number of other investigators have observed similar oxidation products of the derivatives of amino- and diamino-guanidines, but they have not established the constitutions of the substances so obtained. Gaiter (52) observed that *m*-nitrobenzylidenediaminoguanidinium bromide gradually turns to a red substance in the presence of light and air, and Pellizzari and Gaiter (102) found that dibenzylidenediaminoguanidinium nitrate becomes intensely red on exposure to light.

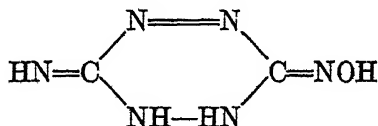
In 1905 Wieland (174) prepared dihydroxyguanidine



in the form of the hydrobromide, from cyanogen bromide and hydroxylamine in methyl alcohol. The material is stable to acids, but alkalis convert it into a deep red substance which had the constitution



Its relationship to azodicarbamide, the initial product of the oxidation of aminoguanidine by acid permanganate, is clearly evident. By continued boiling with dilute acid Wieland and Bauer (175) were able to convert the azo compound to a tetrazine, "isonitrosodihydrotetrazine,"



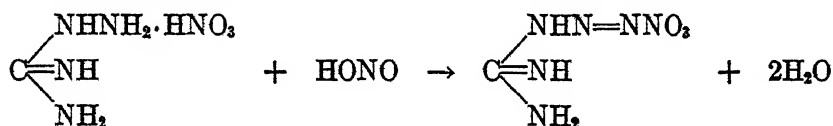
which is closely related to *s*-diaminotetrazine (110), the hydrolytic-oxidative product of free aminoguanidine.

C. Reactions of aminoguanidine with nitrous acid

The products formed by the action of nitrous acid on aminoguanidine are dependent entirely upon the conditions under which the reaction is carried out. In general, aminoguanidine reacts with nitrous acid in three ways: (1) If the reaction is carried out in a solution of a strong mineral acid, guanyl azide is formed; (2) if in aqueous solution alone, aminoguanidine and sodium nitrite form 1-guanyl-4-nitrosoaminoguanilyltetrazene; and (3) if in a solution of acetic acid, ditetrazolyltriazene results. Of these substances guanyl azide has been the most intensively studied, and we shall discuss its formation and reactions first.

1. Formation and reactions of guanyl azide

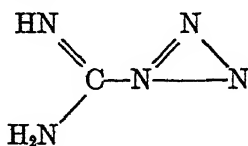
Thiele (147) was the first to prepare guanyl azide as the nitrate, but he believed that the compound was "diazoguanidine nitrate." He came to this conclusion because he considered that the reaction between nitrous acid and aminoguanidine in a solution of a strong mineral acid was a diazotization reaction and should therefore yield a diazo compound.⁵ Thiele believed that the following reaction took place when aminoguanidinium nitrate, dissolved in nitric acid, was treated with sodium nitrite:



The properties of the resulting compound, however, were unusual for a diazonium compound. The substance does not decompose, even when the solution is heated; it does not give off nitrogen even if the solution is boiled; and hydrolysis with a strong alkali gives the corresponding salt of hydrazoic acid. The salts of guanyl azide have an acid reaction, but a diazonium salt with so positive a group as the guanidine residue would be expected to be neutral. The substance is not detonated by shock; on heating it undergoes rapid decomposition with evolution of light and heat but does not detonate. In spite of this strong experimental evidence, Thiele believed this substance to be a true diazoamino derivative containing the group, $-\text{NH}-\text{N}=\text{N}-$.

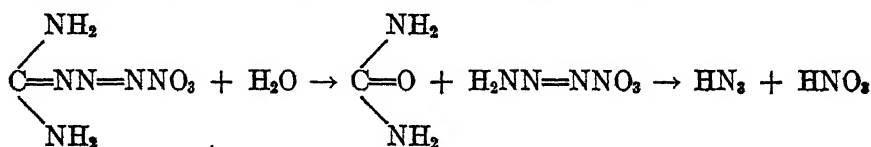
⁵ The formation of guanyl azide from aminoguanidine and nitrous acid is in harmony with the view of Browne and Wilcoxon (J. Am. Chem. Soc. 48, 683 (1936)) that hydrazoic acid may be considered a hydrazinonitrous acid, i.e., a nitrous acid of the hydrazine system. Accordingly, the reaction of nitrous acid with aminoguanidine (a hydrazinoammonocarbonic acid) is an instance of hydrazinolysis of aquonitrous acid. See also reference 41.

Alkaline hydrolysis of guanyl azide leads to the formation of hydrazoic acid (6). Thiele (147) postulated the formation of guanyl azide



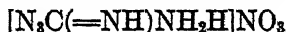
Guanyl azide

as an intermediate compound and considered that its decomposition into hydrazoic acid and cyanamide was favored by the tendency of the hydrazoic acid to form salts. Thiele (147) considered that the intermediate compound "guanyl azide" (triazoguanyl) (61) was only a hypothetical product. He also reasoned that if aminoguanidine possessed the symmetrical structure, then the decomposition of the diazoguanidine would form urea instead of cyanamide, but this was not observed.



The formation of hydrazoic acid from guanyl azide certainly is one of the most interesting transformations of aminoguanidine, and Thiele (146) obtained a patent for this process. He showed that it was not necessary to isolate guanyl azide, but that if the solution obtained by the treatment of an aminoguanidinium nitrate with nitrous acid was refluxed with a solution of sodium hydroxide and then acidified, the hydrazoic acid could be separated by distillation in very high yields. Hydrolysis of guanyl azide with ammoniacal silver yields hydrazoic acid and cyanamide, even in cold solution, but ammonium hydroxide yields a new acid of the composition, CH_2N_5 , which proved to be 5-aminotetrazole (*vide infra*).

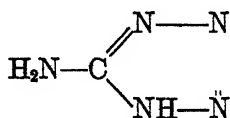
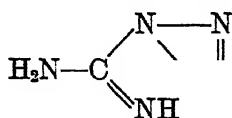
Thiele's (147) so-called "diazoguanidine" of 1892 was reexamined by Hantzsch and Vagt (59) in 1901, who showed that it was not a diazo compound at all but an azide. The fact that it formed a salt was merely due to the presence of the unmodified amino group in the guanidine



XVI

XVI is then the nitrate of carbamideimideazide, or, as recently termed by Hart (61), a nitrate of guanyl azide. The diazoguanidine cyanide (*vide infra*) of Thiele and Osborne (160) appears to favor Thiele's original view, but Hantzsch and Vagt (59) showed that other similar compounds, espe-

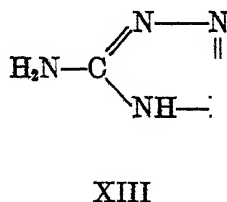
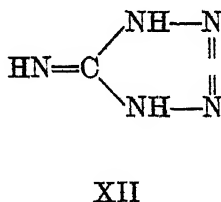
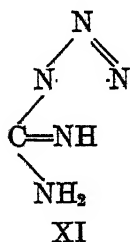
cially carbamyl azide, behaved in the same way. They found also that 5-aminotetrazole can be formed from hydrazoic acid and cyanamide. Accordingly, formation of this substance from Thiele's diazoguanidine, or guanyl azide, may be represented as follows:



5-Aminotetrazole

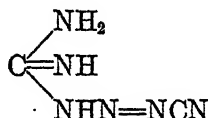
Hantzsch and Vagt (59) further demonstrated that almost a complete analogy existed between the properties of guanyl azide and those of carbamyl azide, the only exception being that the latter does not form a tetrazole ring.

The action of solutions of weak bases (ammonium hydroxide, for example) or of solutions of weak acids on guanyl azide resulted in ring closure, perhaps a hydrolytic reaction; a new compound, CH_3N_5 (a monobasic acid), was formed. Thiele (147) gave the name "aminotetrazoic acid" to this substance, since it would form salts with barium, sodium, and silver.



Thiele at once rejected formula XI, because of the properties of the new compound. Nitrous acid converted it into a material which could not be isolated because of its explosive properties. It was a diazonium compound, however, because it coupled with dimethylaniline or β -naphthylamine to form definite azo compounds. On this basis Thiele rejected formula XII. Substances having the ring CN_4 had been prepared, and their properties had been described previously by Lossen (82) and Bladin (9). Because of the analogous behavior of CH_3N_5 , Thiele (147) assigned formula XIII as representing the constitution for "aminotetrazoic acid" and termed its formation an "intramolecular diazoamino condensation." On this basis, therefore, the modern name would be 5-aminotetrazole. Potassium cyanide, "diazoguanidine nitrate," or guanyl azide react and

form a substance to which Thiele and Osborne (160, 161) assigned the formula



and which they called diazoguanidine cyanide. As the compound contains the chain $\text{N}-\text{N}=\text{N}$, it is the *first representative of an aliphatic diazoamino compound*. It may also be considered as a substitution product of the hypothetical $\text{HN}=\text{N}-\text{NH}_2$, "triazene." Denoting the group,

$\text{HN}=\text{C}-\text{NH}_2$, as "aminoiminomethyl," Thiele and Osborne (161) accordingly named the compound "aminoiminomethylcyantriazene," but we shall refer to it by the modern name (1-guanyl-3-cyanotriazene). A number of reactions which are characteristic of the cyano group led to the formation of a whole series of substituted triazenes.

Mild hydrolysis in acidic solution converts the cyano group to the carbamyl group, $-\text{CONH}_2$, and accordingly yields "aminoiminomethyltriazenecarbamide" (1-guanyl-3-carbamyltriazene)



Hydroxylamine converts this compound into a "triazenedicarbamidinamidoxime" or 1-guanyl-3-amidoximetriazene:



This substance, on warming with water, is converted into 5-aminotetrazole and a very hygroscopic substance, which was not further identified (2). An imino-ether (a mixed ammonoaquo ester) is formed by the action of alcohol in an acidic solution,



and this ester is hydrolyzed in the presence of hydrochloric acid, yielding an ester:



The imino-ether is ammonolyzed to an amidine, "triazenedicarbondiamidine" or 1,3-diguanyltriazene:



The aliphatic diazoamino compounds prepared as described above are yellow crystalline materials. With acids they form well-characterized salts which are nearly all white and very soluble in water. The solutions

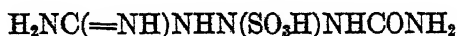
of these salts give an acidic reaction, indicating thus that the compounds are salts of weak bases. On heating the aqueous solutions of the salts, decomposition with evolution of nitrogen results. An alkaline solution of ferrous salts gives to the solutions an intense reddish violet to a red-brown color, which is quickly destroyed by oxidation in air. The melting points of these compounds are of no significance since the compounds explode, especially in a confined tube, and the temperature of their decomposition by detonation depends upon the rate of heating. They resemble the aromatic diazoamino compounds in giving off two-thirds of the triazene nitrogen on being heated with dilute acids, but they differ from them (1) in being decomposed by alkalis to which the aromatic compounds are unreactive, and (2) in being unaffected by cold concentrated acids.

Thiele and Osborne (162) also succeeded in reducing these triazenes to triazanes, i.e., hydrazoamino compounds. Like so many substances with doubly linked nitrogen, the triazenes react with sulfurous acid and form the sulfonic acids of the reduced compounds. Since the products no longer behave as a diazoamino substance, the reduction must have taken place in the triazene group. Therefore the question to be answered is whether the SO_2H group goes to the 2- or the 3-position, i.e., whether the product is



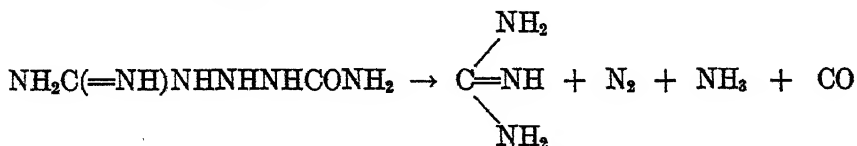
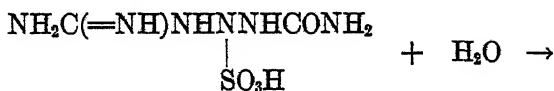
XIV

or



XV

If the resulting substance were XIV, it would be readily oxidized to a diazoamino derivative; it is, however, not easily oxidized and therefore must be XV. All attempts to replace the SO_3H group with hydrogen failed. If the substance is heated with acids, sulfuric acid is formed, but the triazane which must be produced decomposes and nitrogen, carbon monoxide, guanidine, and other products are formed.



Attempts were also made to reduce the diazoamino compounds directly. Under ordinary circumstances this gives, as it does in the aromatic series, an amine and a substituted hydrazine. But when the substance was carefully reduced with zinc dust and ammonium chloride, a colorless solution was obtained which gave no reaction for the triazene. The product must contain the nitrogen chain, since on oxidation the diazoamino compound is re-formed. The solution has strong reducing properties, and on warming readily decomposes into the same substances as are obtained by removing sulfuric acid from the sulfonic acid (XV). Thiele and Osborne (162) concluded, therefore, that in both cases the true triazane derivative

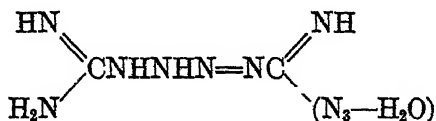


is formed, but that it is too unstable to be isolated. This instability of this substance makes it seem unlikely that any attempts to prepare free triazane, H_2NNHNH_2 , will be successful.

2. Formation and properties of 1-guanyl-4-nitrosoaminoguanylisotetrazene

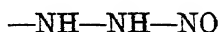
The versatility of aminoguanidine is abundantly demonstrated by the different products which it forms with nitrous acid. We have already discussed the formation of guanyl azide in a solution of a strong acid. If sodium nitrite is allowed to react with aminoguanidinium nitrate, in aqueous solution only, for 6 to 7 days at a temperature of 0°–10°C., a very different reaction product results. This product is a white crystalline compound of the composition $C_2H_7N_{10}OH$ (70). Investigations have established it as being 1-guanyl-4-nitrosoaminoguanylisotetrazene. Hofmann and Roth (70) found that the compound formed salts which were readily hydrolyzed, and that these salts were often extremely explosive; this was true particularly of the perchlorate. Four atoms of nitrogen are liberated when an aqueous solution of the compound is heated to the boiling temperature. This indicates that two diazo groups are present, one of which probably bridges the two carbon atoms as a diazoamino chain, while the other exists as an isodiazohydrate group.

Further investigation by Hofmann, Hock, and Roth (69) indicated that the probable constitution was as follows:



The nitrogen bridge between the carbon atoms comprises a diazohydrazo or *as*-tetrazene ("buzylene") group, and the compound is a substituted

isotetrazene. The radical ($\text{N}_3\text{—H}_2\text{O}$) was believed to be present either as a free nitrosoamino

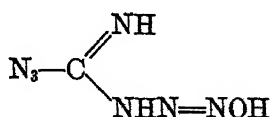


or as an antidiazohydrate group



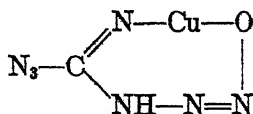
For these reasons they called the substance "guanylnitrosoaminoguanilyltetrazene" or "guanyldiazoguanilyltetrazene." The substance was found to be unattacked by concentrated aqueous ammonia at ordinary temperature. It is not reactive with aqueous solutions of potassium cyanide (10 per cent) or mineral acids of the same concentration. It is neutral to litmus, and with α - and β -naphthols it yields brownish to yellowish red products. It forms salts rather slowly, and therefore it was regarded as a pseudo base.

Evidence for the constitution of guanyldiazoguanilyltetrazene was obtained by submitting it to alkaline hydrolysis and making a comparison of the products with those obtained from the alkaline hydrolysis of a tetrazene (hippurylphenylbuzylene) previously discovered by Curtius (22). The products obtained from guanyldiazoguanilyltetrazene on hydrolysis with aqueous sodium hydroxide were ammonia, cyanamide, and triazonitrosoaminoguanidine:

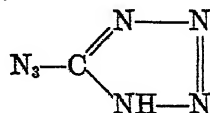


Triazonitrosoaminoguanidine

This substance could be obtained only in the form of the copper salt,



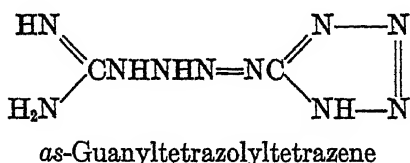
On acidification, triazonitrosoaminoguanidine was converted into tetrazolyl azide (5-azidotetrazole).



5-Azidotetrazole

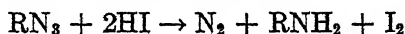
This substance was described previously by Thiele and Ingle (157). In order to demonstrate (69) that the guanyldiazoguanilyltetrazene, $\text{C}_2\text{N}_{10}\text{H}_8\text{O}$,

contains no tetrazole ring, an *as*-guanyltetrazolyltetrazene was prepared from aminoguanidine and diazotized 5-aminotetrazole in acetic acid solution:



While this substance gave the same products on alkaline hydrolysis, it differed so markedly in other physical and chemical properties from guanyldiazoguanilyltetrazene, that there was no doubt that the tetrazole ring was absent from this latter substance. It is of interest to note that Thiele (147), in his early studies, had already obtained the guanyltetrazolyltetrazene, but he was not able to establish its constitution.

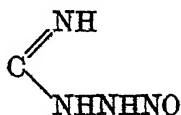
Hofmann, Hock, and Kirmreuther (68) continued the study of the structure of guanyldiazoguanilyltetrazene, since the exact structure of the ($\text{N}_3\text{---H}_2\text{O}$) radical was still not established. The evidence (69, 70) that it did not contain a tetrazole ring has been described. The question to be answered was, "Is the radical ($\text{---C(=NH)N}_3\text{---H}_2\text{O}$) a hydrate of an azide?" These investigators found that the substance did not lose weight on drying in a vacuum over phosphorus pentoxide and that it formed salts without additional water of hydration even from aqueous solutions. It was therefore concluded that the substance did not contain water of crystallization. The following reaction characteristic of the azido group was used in testing for the presence of the azide radical:



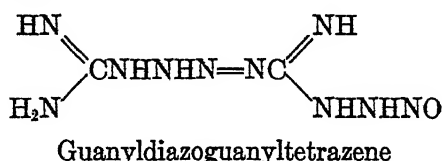
It was found that the substance $\text{C}_2\text{H}_8\text{N}_{10}\text{O}$ formed a salt of the composition $\text{C}_2\text{H}_7\text{N}_{10}\text{I}$, and the original substance could be obtained by treating the salt with aqueous ammonia or a solution of sodium acetate. The azide group was therefore absent. From the previous work it was known that the salt formation occurred through an oxygen base rather than an amino-basic linkage. Thus, for example, an excess of silver nitrate gives the salt



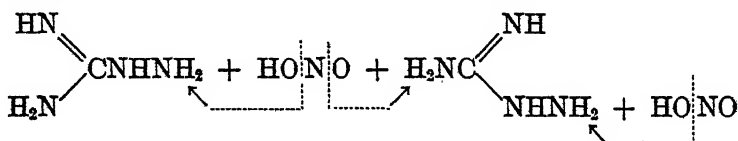
suggestive of the isodiazotate group. The evidence was, therefore, conclusive that the radical ($\text{N}_3\text{---H}_2\text{O}$) is a β -nitrosohydrazine



The β -position for the nitroso group is indicated by the conversion of this group to a tetrazole ring (69). The structure of guanyldiazoguanyl-tetrazene is, therefore, as follows:

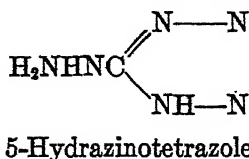


The mechanism of its formation is indicated below:

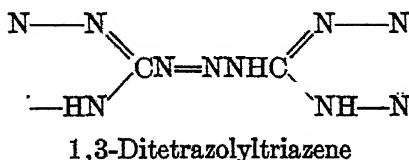


3. Formation and properties of 1,3-ditetrazolyltriazene

Hofmann and Hock (66) investigated the action of aminoguanidinium nitrate and sodium nitrate in an aqueous solution of acetic acid and found that 1,3-ditetrazolyltriazene was formed. This substance had the empirical composition, $\text{C}_2\text{H}_2\text{N}_{11}$, and was obtained in the form of almost colorless, lustrous, thin, doubly refractive plates, containing one molecule of water of crystallization. It possessed well-marked acidic properties and could be titrated to secondary salts in the presence of indicators. When boiled with dilute acids, it formed nitrogen and 5-aminotetrazole. In the presence of alkali, it gave a golden-yellow solution with β -naphthol. In dilute sulfuric acid it combined with seven atoms of oxygen from potassium permanganate. Since reduction with zinc and hydrochloric acid gave 5-aminotetrazole and tetrazolyldiazene (5-hydrazinotetrazole)

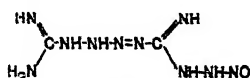


the structure was concluded to be the following:



Its formation was explained as follows: Under the environmental conditions of the reaction medium, the aminoguanidine is converted into

Thiele's (147) "guanyl azide" which, in turn, is immediately isomerized into 5-aminotetrazole. This is subsequently diazotized in part and then

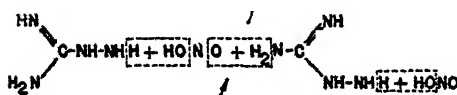


1-GUANYL-4-NITROSOAMINO GUANYLISOTETRAZENE

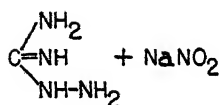
GUANYLNITROSO GUANYLTETRAZENE



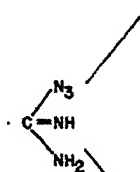
HYDRAZOIC ACID



ABSENCE OF
ACID

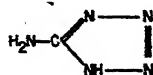
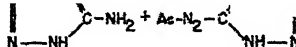
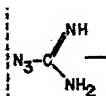


ACETIC ACID



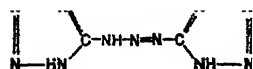
GUANYLAZIDE

ACID &
WEAK BASES



5-AMINOTETRAZOLE

"AMINOTETRAZOLIC ACID"



DITETRAZOLYLTETRAZENE

"DIAZOAMINOTETRAZOLIC ACID"

FIG. 1. Schematic summary of the reactions between aminoguanidine and nitrous acid

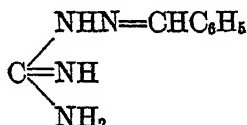
coupled with the remainder to form the very slightly soluble primary sodium salt of the 1,3-ditetrazolyltriazene.

4. Summary of the reactions between aminoguanidine and nitrous acid

The researches of Thiele (147), Hantzsch (59), and Hofmann (66, 68, 69, 70) on the reaction of aminoguanidine with sodium nitrite may be summarized as follows: (1) In the absence of acids guanyldiazoguanyl-tetrazene is formed. (2) In the presence of mineral acids guanyl azide is formed, which may be converted by alkali to hydrazoic acid or isomerized to aminotetrazolic acid by acids or weak alkalies. (3) With acetic acid diazoaminotetrazolic acid is formed.

D. Reaction with carbonyl compounds without ring formation

As a substituted hydrazine, aminoguanidine is capable of combining with aldehydes and ketones with elimination of water. Thiele (147) prepared the first compound of this type, the benzaldehyde derivative,



Benzaldehyde guanyldiazone

by treating an aminoguanidine salt with benzaldehyde in a concentrated solution of potassium hydroxide. The guanyldiazone separates as pearly leaflets, readily recrystallizable from toluene and having a melting point of 178°C. Thiele and Bihan (154) found later that the condensation with carbonyl derivatives took place much better in acid media. The aminoguanidine salt is treated with an aqueous or alcoholic solution of the carbonyl compound to which has been added a few drops of a mineral acid and the salt of the condensation product separates in very pure form.

Wolff (177, 178) studied the application of aminoguanidine to the formation of guanyldiazones of the sugars. From galactose and glucose beautiful crystalline condensation products were obtained. Baeyer (8) made several terpene derivatives and isolated the picrates of the guanyldiazones.

Thiele and Dralle (155) studied a number of condensation products of aminoguanidine with aldehydes and ketones of the aliphatic series. With monochloro- and trichloro-aldehydes the normal hydrazones were first obtained,



and



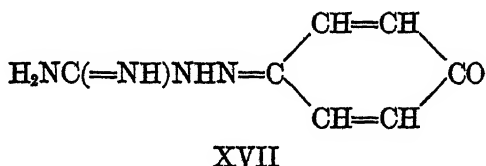
which were unstable. The trichloro product was easily converted, with loss of hydrogen chloride, into the guanyldiazone of glyoxylic acid:



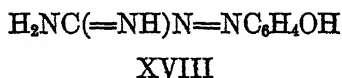
α -Diketones and similar compounds were found to yield only osazones. The formation of monohydrazones with closure to six-membered rings was not observed in the aliphatic series.

Thiele and Bihan (154) studied the condensation of aminoguanidine with some aromatic aldehydes and ketones. The *o*- and *p*-hydroxybenzaldehydes and the three nitrobenzaldehyde derivatives were prepared. All these compounds exhibited properties similar to those of benzalaminoguanidine. The nitrobenzalaminoguanidines, beautiful red to yellow crystals, were found to be very strong bases. It is interesting to note that the *o*- and *p*-nitrobenzalaminoguanidines could be made by the nitration of benzalaminoguanidine.

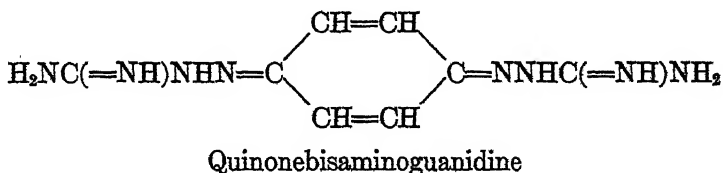
In 1898 Thiele and Barlow (153) reported on a detailed study of the condensation of aminoguanidine with quinones. The condensation takes place readily in the presence of a trace of nitric acid. Intensively colored nitrates are formed, from which the yellow to red bases are readily isolated.



These compounds appear to exist in a tautomeric form as hydroxyazo derivatives (XVIII):

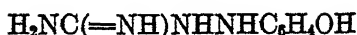


Benzoquinone guanyldiazone, on treatment with an additional mole of aminoguanidine salt, is easily converted into quinonebisaminoguanidine,

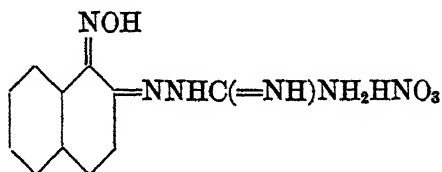


giving evidence for the existence of the quinone form (XVII). On reduction, both the mono- and di-derivatives are converted into guanyldiphenyl-

hydrazines. Benzoquinone guanylhyazone yields 1-guanyl-2-(*p*-hydroxyphenyl)hydrazine,

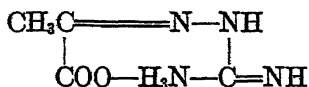


which on oxidation is readily converted back to the original substance. α -Naphthoquinone was found to behave in an analogous manner to quinone. β -Naphthoquinone, however, yielded only a mono-derivative which could be distinguished from the α -quinone by its insolubility in alkali. On alkaline hydrolysis, β -naphthoquinone guanylhyazone yields α -naphthol, indicating that the aminoguanidine residue is combined with the β -carbon atom. Quinone monooximes were found to condense with aminoguanidine to yield very unstable derivatives. Nitroso- β -naphthol formed a well-characterized nitrate of nitroso- β -naphthol guanylhyazone.

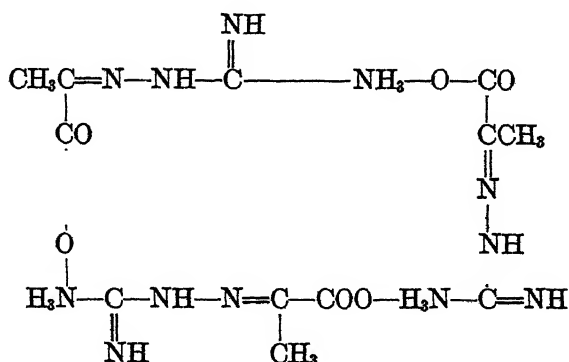


Hydrolysis in boiling water yields ammonium nitrate and a substance of the composition $\text{C}_{11}\text{H}_8\text{N}_4\text{O}$, having both acid and basic properties and forming well-crystallized salts with acids. Reduction forms a new compound of the composition $\text{C}_{11}\text{H}_8\text{N}_4$, which is only basic. No structures were given for these substances.

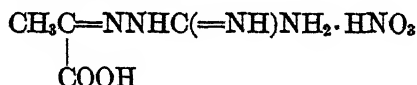
Following the pioneering work of Thiele and his students, many investigators have utilized this property of aminoguanidine for the preparation of derivatives of a large variety of substances. Doebner and Gartner (34) describe the aminoguanidine derivative of glyoxylic acid and Stoermer (137) that of phenoxyacetone; aminoguanidine derivatives have been prepared by Steinkopf and Schubart (134) for thienyl ketones, by Müller (89) for pyrrolealdehydes in a study of the constitution of the bile acids, by Rojahn and Trieloff (124) for triazolealdehydes, by Rojahn and Kühling (121) for pyrazolealdehydes, by Rojahn and Schulten (123) for thiophenealdehydes, by Rojahn and Rühl (122) for a cyclopentanone derivative, by Conard and Shriner (20) for *p*-dimethylaminobenzaldehyde, and by Degiorgi (31) for fluorenone and nitrofluorenone. Wedekind's (170) investigation of the aminoguanidine condensation product with pyruvic acid is of considerable interest. The free base was assumed to be an inner salt:



However, molecular weight determinations indicated a polymeric substance corresponding to a trimer, which was assumed to have the constitution:



The polymeric product is regenerated by mineral acids. On gentle warming with nitric acid, the normal salt



is formed with all its original properties. The condensation product forms salts in alkaline solution. By double decomposition of the ammonium salt with silver nitrate, an explosive silver salt is formed, containing silver atoms both in the carboxyl and hydrazine portions of the molecule.

The substituted aminoguanidines also form well-characterized derivatives with aldehydes and ketones. Busch and Bauer (16) describe a number of such derivatives of their diarylaminoguanidines. A very complete study of the condensation of diarylaminoguanidines with phenanthraquinone has recently been presented by De and Dutta (28). Pellizzari and Roncagliolo (103) describe the acetaldehyde, the chloral, and the acetoacetic ester derivatives of aminophenylguanidine. Pellizzari and Gaiter (102) and Gaiter (52) describe the carbonyl derivatives of diaminoguanidine. Fromm and students (45, 48, 50) describe a number of carbonyl derivatives of their (aminoguanyl)arylthioureas. Phillips and Williams (107), Whitmore, Revukas, and Smith (173), and Smith and Shoub (133) have studied extensively the carbonyl derivatives of nitroaminoguanidine.

V. SYNTHESSES FROM AMINOGUANIDINE

Nitrogen and hydrogen form a series of compounds which are analogous to the hydrocarbons, the silanes, the germanes, and the boranes, but nitrogen appears to have a lesser tendency than does carbon, silicon,

germanium, or boron to enter into chain formation. Only three compounds that are true free hydronitrogens are known—ammonia, hydrazine, and hydrogen azide. Organic derivatives of other hydronitrogens have long been known, but many of them are relatively unstable.

It is therefore of important theoretical interest to observe that syntheses starting from aminoguanidine have led to the formation of nitrogen chains containing three, four, six, and seven nitrogen atoms, and these compounds have been found relatively stable. In this respect they differ markedly from the aromatic substituted hydronitrogens, many of which are relatively unstable. The properties of these substituted higher hydronitrogens, which are reviewed and discussed here, should be given more consideration than in the past in drawing general conclusions regarding the relative stability of nitrogen chain compounds.⁶

The heterocyclic nitrogen compounds which are formed from aminoguanidine and from its derivatives also have properties which are unusual in many respects. Cyclizations have been accomplished by reactions of aminoguanidine with carboxylic acids, diketones, keto esters, and nitrous acid. Such reactions have involved hydrazination followed by deamination, and pyrolysis involving deamination, dehydrazination, removal of arylamines, and removal of hydrogen sulfide. Some of the reactions appear to be intramolecular ammonation or hydrazination. We shall discuss these heterocyclic compounds in classes, grouped according to the number of nitrogen atoms in the ring and the total number of atoms in the ring.

A. *The higher hydronitrogens*

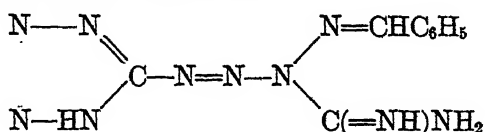
The reaction products of aromatic diazonium salts and hydrazines which form diazohydrazides or derivatives of isotetrazene, $RN=NNHNHR$, were shown by Fischer (38), Curtius (22), Wohl (176), and Dimroth (33) to be very unstable substances. They decompose at ordinary temperature into azides and amines, or into phenols, nitrogen, and hydrazine. No diazohydrazides could be prepared from hydrazine itself. It is, therefore, of great practical and theoretical interest to point out that the diazohydrazides obtained by Hofmann and his students from aminoguanidine (66, 69, 70) were all found to be exceptionally stable substances. In addition to the work already cited, Hofmann and Hock (67) studied the condensation of diazotized 5-aminotetrazole with hydrazines for the purpose of contributing to our knowledge of the existence and reactivity of compounds containing chains with four atoms of nitrogen, the so-called

⁶ Compare, for example, Sidgwick's *Organic Chemistry of Nitrogen*, p. 457, Taylor and Baker, Oxford (1937).

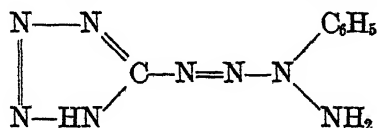
isotetrazenes or buzylenes of the structures $RN=NNHNHR$ (the unsymmetrical tetrazenes) or $RN=NN(R)NH_2$.

The preparation of guanyltetrazolyltetrazene has already been described (69). It did not hydrolyze on exposure to moist air for one week at room temperature. It did not react with precipitated mercuric oxide at ordinary temperature; with Fehling's solution it evolved nitrogen; and no reaction took place with benzaldehyde. Alkaline hydrolysis produced cyanogen, nitrogen, aminoguanidine, and 5-aminotetrazole.

Diazotetrazolybenzalamino-guanidine



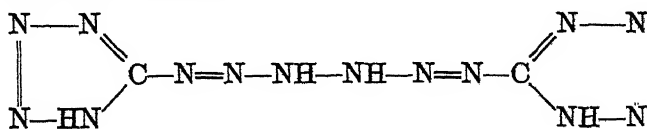
was prepared by adding diazotetrazole to a solution of benzalamino-guanidine containing acetic acid. It precipitated as an intensely orange-red substance. It was stable at room temperature and did not decompose until 132°C . Acid hydrolysis yielded nitrogen, cyanogen, benzaldehyde, and hydrazine. Most interesting was its behavior toward alkalis. Addition of concentrated sodium hydroxide precipitated orange-red needles which redissolved at 90°C . to form a reddish yellow solution capable of being kept at this temperature for a long time without decomposition. On cooling and acidifying, the original substance was recovered unchanged. Diazotetrazolyphenylhydrazide



Diazotetrazolyphenylhydrazide

prepared from 5-aminotetrazole and phenylhydrazine, was found to behave in an analogous manner.

Bisdiazotetrazolyhydrazide

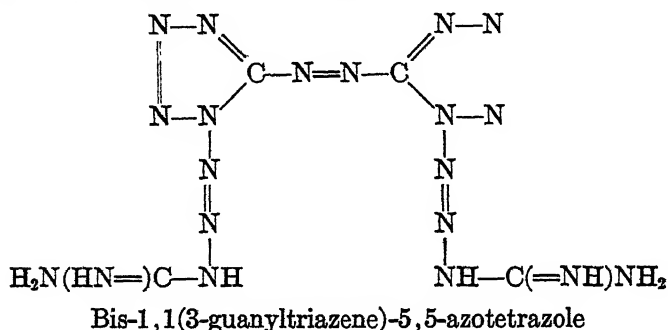


Bisdiazotetrazolyhydrazide

is of particular and considerable interest since, contrary to statements of previous workers, it represents the *first diazohydrazide isolated from hydrazine* itself and, moreover, there is present a *stable chain of six nitrogen atoms*.

It was prepared by adding diazotetrazole to a solution of hydrazine hydrochloride in the presence of sodium acetate at low temperature. It forms doubly refractive flakes. It is stable at 25°C., but explodes violently at 90°C. or when pressed with a glass rod. Hydrolysis in aqueous solution yields nitrogen, 5-aminotetrazole, and tetrazolyl azide, while acid hydrolysis furnishes cyanogen, nitrogen, ammonia, and tetrazolyl azide. Addition of cold concentrated alkali first yields a precipitate of intensely yellow plates of the sodium salt, which on dilution with water evolves nitrogen; 5-aminotetrazole and tetrazolyl azide remain in the solution.

Thiele (152), in a paper on azo and hydrazo derivatives of 5-amino-tetrazole, reported the preparation of "azotetrazolylbisdiazoguanidine" (bis-1,1(3-guanyltriazene)-5,5-azotetrazole),

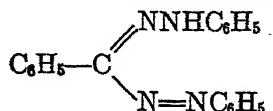


from guanyl azide and sodium azotetrazole. This compound is a yellow, crystalline powder. It decomposes in warm water with evolution of gas. It is of special interest because it probably is the only substance in which there are present *two chains of seven nitrogen atoms*.

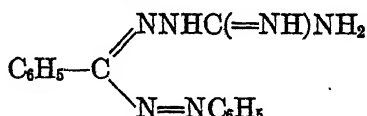
In order to demonstrate further the structure of the diazohydrazides described in the foregoing, Hofmann and Hock (67) studied the condensation of diazotetrazole with hydrazine-free substances, such as guanidine and dicyandiamidine. In both cases only the guanidine and dicyandi-amidine salts of diazoaminotetrazole were isolated. This showed that when diazotetrazole was condensed with such hydrazides as aminoguanidine, the coupling took place only through the hydrazine portion of the molecule and not in the imino or amino groups.

B. The guanazyls

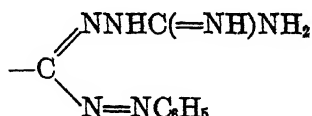
Pechmann (92), in 1894, showed that the tertiary hydrogen atom in benzaldehyde phenylhydrazone is reactive; for example, with diazobenzochloride it reacts and forms derivatives of the type



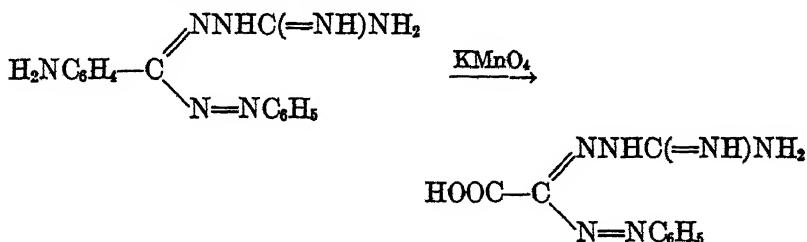
which he termed "formazylbenzoyl." The reaction takes place only in the presence of strong alkali. Wedekind (165), in 1897, investigated the effect of replacing the phenylhydrazine radical by a strongly basic substance, with the assumption that this would permit a more direct formation of the formazyl derivatives. For this purpose he used aminoguanidine. A dilute alcoholic solution of benzalaminoguanidine reacts with an aqueous solution of a diazonium salt to give



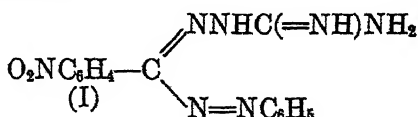
The radical



was termed "guanazyl." These compounds, orange-red to yellow in color, were found to be extremely stable. Either phenyl radical could be nitrated; the resulting nitro derivatives could be reduced to amines, which subsequently could be diazotized and coupled to other aromatic compounds to form complicated azo bodies. They are not easily oxidized; however, if an amino group is present on one of the benzene rings, the oxidation proceeds rapidly as follows:

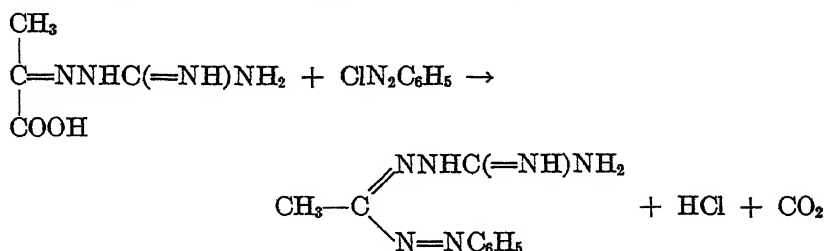


and guanazylformic acid is formed. The guanazyls do not form salts even with strong acids. Wedekind (165) also demonstrated that substituted benzalaminoguanidines react similarly; *p*-nitrobenzalaminoguanidine yields *p*-I-nitroguanazylbenzene

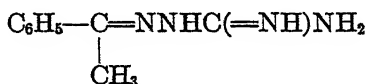


while *o*-benzalaminoguanidine (169) gave the corresponding *o*-I-hydroxy-guanazylbenzene. In 1899 Wedekind (170) prepared the simplest type of

guanazyl from the reaction of the condensation product of pyruvic acid with aminoguanidine and diazobenzenechloride



The compound formed was guanazylmethane. In order to demonstrate that the diazonium chloride coupled through the hydrogen atom attached to carbon and not to nitrogen, Wedekind (170) prepared a compound of aminoguanidine in which the hydrogen atom involved was not present. Such a compound

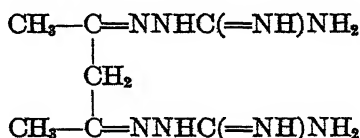


the succeeding homolog of benzalaminoguanidine, was obtained from acetophenone. This compound did not react with diazobenzoehchloride.

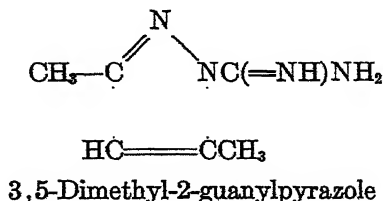
C. Heterocyclic compounds

1. Five-membered rings

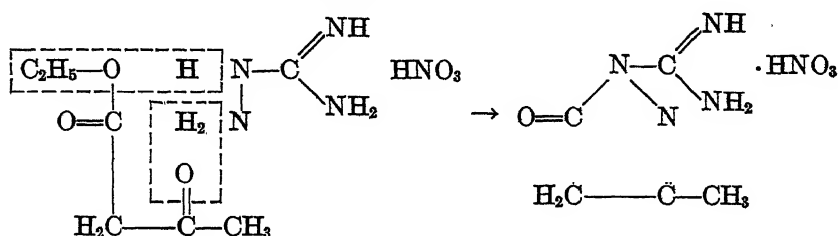
(a) *Pyrazoles*. Thiele and Dralle (155) found that aminoguanidine reacted with acetylacetone, a β -diketone, to form the dihydrazone



and this compound was converted to 3,5-dimethyl-2-guanylpurazole



with the elimination of aminoguanidine; the formation of a monohydrazone was not observed. De and Rakshit (30) have studied the condensation of aminoguanidine and diarylamino-guanidines, ArNHC(=NAr)NHNH_2 , with β -ketonic esters and β -diketones. In all cases well-defined pyrazole and pyrazolone derivatives were isolated. The method of carrying out the reaction consists simply in mixing concentrated solutions of the reactants in water or alcohol at room temperature. On standing, the pyrazole or pyrazolone separate as insoluble products. For example, ethyl acetoacetate and aminoguanidinium nitrate yield 3-methyl-pyrazolone-1-carbamidine nitrate

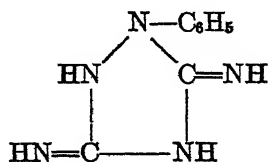


m.p. 234°C . In some cases the mono- or di-hydrazones are isolated. For example, ethyl benzoylacetate and aminoguanidinium nitrate yield ethyl benzoylacetoaminoguanidinium nitrate



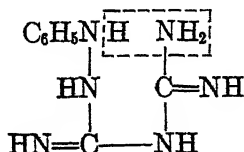
which on cyclization gives 3-phenylpyrazolone-1-carbamidine nitrate, m.p. 190°C . The original paper (30) should be consulted for details about numerous other derivatives in this series.

(b) *Triazoles*. Pellizzari (93), in 1891, attempted to prepare phenyl-aminobiguanide by the reaction of phenylhydrazine hydrochloride with dicyandiamide, but this product was not obtained. When equal molecular quantities of both substances were heated to 150°C ., a vigorous reaction ensued with evolution of ammonia, and a base of the composition $\text{C}_8\text{H}_8\text{N}_8$ was isolated. This was shown to be phenylguanazole, or 1-phenyl-3,5-diaminodihydrotriazole

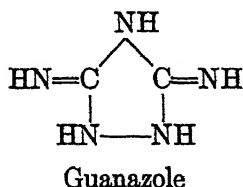


1-Phenyl-3,5-diaminodihydrotriazole

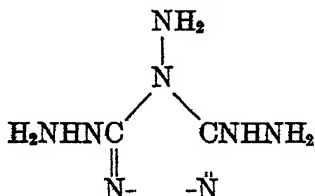
in which it was assumed that the phenylaminobiguanide



first formed subsequently lost ammonia in closure to the triazole ring. As proof of this mechanism, Pellizzari (93) showed that *as*-ethylphenylhydrazine did not give the same reaction. As additional confirmation it was found that phenylaminoguanidinium chloride reacts with either cyanamide or guanidine to give phenylguanazole. Similarly it is also formed from phenylhydrazine and biguanide. In the reaction of molar quantities of dicyandiamide with hydrazine hydrochloride in 15 parts of 90 per cent alcohol in a pressure flask at 100°C., Pellizzari (93) found that guanazole

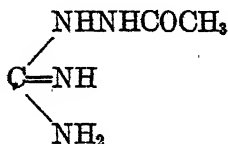


was the principal product. Its formation can readily be explained on the same basis given for phenylguanazole. Stollé and Krauch (143) found that the reaction of 10 g. of dicyandiamide with 25 g. of hydrazine hydrate at 67°C. gave a substance which formed rose-colored leaflets on recrystallization from alcohol. This substance was shown to have the structure

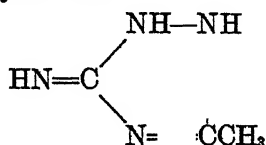


and was called "dihydrazidoaminotriazole."

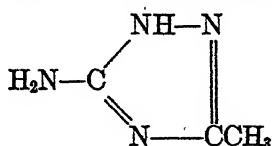
Thiele (147) found that aminoguanidine reacts with acetic acid to form, probably, acetylaminoguanidine



This substance on warming or treatment with alkali lost a molecule of water and formed an inner anhydro base:

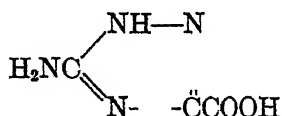


Thiele and Heidenreich (156) found that the substance $\text{C}_3\text{H}_6\text{N}_4$ had the properties of an acid. On oxidation an azo derivative was formed; other work showed that an amino group capable of diazotization was present. Accordingly the product was aminomethyltriazole.



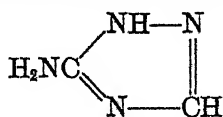
Aminomethyltriazole

Thiele and Manchot (158) showed that the reaction leading to the formation of aminomethyltriazole was general for all acid derivatives of aminoguanidine. For example, oxalylaminoguanidine is converted into aminotriazolecarboxylic acid,



Aminotriazolecarboxylic acid

and from formylaminoguanidine, aminotriazole



Aminotriazole

is obtained. Franklin and Bergstrom (41) have recently termed this "the elimination of water from an open-chain carbonic acid acyl hydrazide." Reilly and Madden (118) have prepared the corresponding ethyl, isopropyl, and isobutylaminotriazoles; Reilly and Drumm (116) prepared the *n*-propylaminotriazole. Manchot (84) and Manchot and Noll (85) have prepared a number of derivatives of aminotriazoles from aminoguanidine. Fantl and Silbermann (36), in repeating the preparation of methylaminotriazole by the method of Thiele and Heidenreich (156), observed that the alkaline solution took on a deep violet color. Closer

any base having the foregoing group and belonging to an unsaturated cyclic system is necessarily diazotizable. The absence of diazotizability is noteworthy in the thiophene, furan, and pyrrole series, in spite of the close relationship between the first of these series and the aromatic compounds.

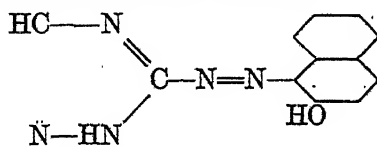
The much greater stability of diazotized aminodimethylpyrazole in comparison with the corresponding unalkylated compound (117) led Reilly and Drumm (116); Reilly and Madden (118), and Reilly and Caldwell (115) to an investigation of the diazotization of the higher aminoalkyl-triazoles from aminoguanidine. It was found that the stability of the triazolediazonium salts was increased by alkyl substitution, the effect increasing with the molecular weight of the alkyl group. The comparative

TABLE 1
Comparative stability of alkyltriazolediazonium salts

| ALKYLTRIAZOLE | VOLUME OF GAS EVOLVED IN 15 MIN. | | VOLUME OF GAS EVOLVED IN 20 MIN. | |
|---|-------------------------------------|----------|-------------------------------------|----------|
| | Nitrate | Chloride | Nitrate | Chloride |
| | ml. | ml. | ml. | ml. |
| 5-Amino-1,2,4-triazole..... | 22.0 | 27.7 | 26.8 | 33.1 |
| 5-Amino-3-methyl-1,2,4-triazole..... | 19.5 | 22.1 | 23.2 | 28.4 |
| 5-Amino-3-ethyl-1,2,4-triazole..... | 19.0 | 22.0 | 23.0 | 30.8 |
| 5-Amino-3-isopropyl-1,2,4-triazole..... | 18.1 | 19.4 | 23.6 | 26.8 |
| 5-Amino-3-isobutyl-1,2,4-triazole..... | 13.1 | 16.6 | 19.2 | 26.1 |

stability may be judged from table 1, which gives the milliliters of gas evolved from 0.002 gram-mole of the various triazolediazonium salts at 55°C. in the presence of 6 moles of acid. Compared with benzenediazonium salts, the diazonium nitrates and chlorides from these aminoalkyl-triazoles show pronounced stability.

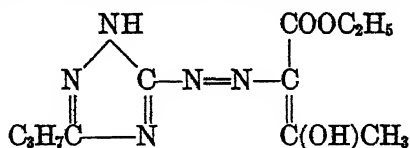
The diazonium salts readily yield azo dyes with β -naphthol, β -naphthylamine, and related aromatic substances. Unlike the purely aromatic azo- β -naphthols, 1,2,4-triazole-5-azo- β -naphthol



1,2,4-Triazole-5-azo- β -naphthol

is soluble in dilute aqueous alkali hydroxides (88). This solubility is in all probability due to the presence in the triazole ring of an imino group contiguous to the carbon atom bearing the azo complex. That the

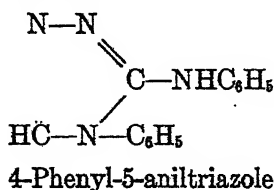
hydroxylic hydrogen of the aromatic group is not involved in this salt formation Morgan and Reilly (88) demonstrated by the fact that 1,2,4-triazole-5-azo- β -naphthylamine is also readily soluble in aqueous alkali hydroxides. The acidic character of the iminic hydrogen atom probably also plays an important part in determining the transformation of these diazonium compounds into isodiazio derivatives. They also couple with β - and γ -keto-esters and diketones to yield azo compounds. For example (116), ethyl 3-propyl-1,2,4-triazole-5-azoacetoacetate



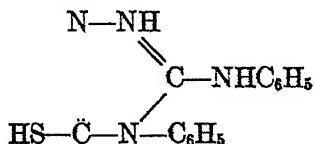
Ethyl 3-propyl-1,2,4-triazole-5-azoacetoacetate

is formed from the diazonium nitrate and ethyl acetoacetate. This represents the *first time that azo-condensation products of β -diketones and keto-esters (116) have been isolated*, although Bülow, in 1909, had prepared similar products from diazotized aminotetrazolic acid (13). These products are of considerable interest in connection with the relation between color and constitution, as they represent azo structures in which no aromatic residue is present.

Busch and Bauer (16) found that no formyl or acetyl derivatives of their diarylaminoguanidines could be isolated, but they found that ring closure takes place directly to form derivatives of triazole. For example, diphenylaminoguanidine and formic acid yield 4-phenyl-5-aniltriazole,



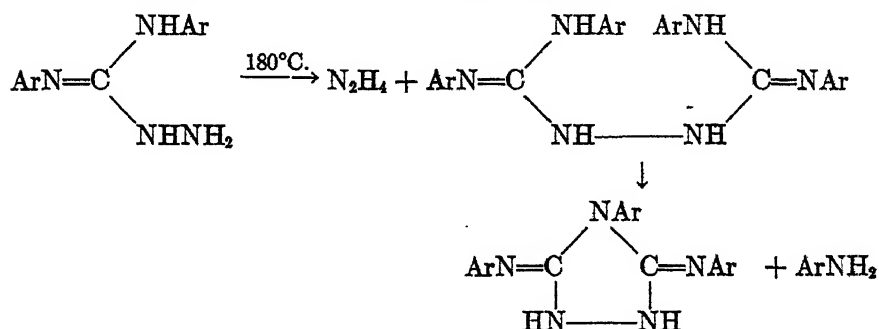
and the same product was obtained by reaction with oxalic acid, with loss of carbon dioxide (18). In the formation of diphenylaminoguanidine (16) two by-products were isolated. The first, a beautiful crystalline sulfur-containing acidic substance, was shown by Busch and Ulmer (18) to be 4-phenyl-5-anil-3-thioltriazolone



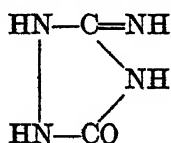
and to be formed by the reaction of diphenylaminoguanidine with excess thiocarbanilide, yielding as intermediate diphenyl(aminoguanido)phenylthiourea



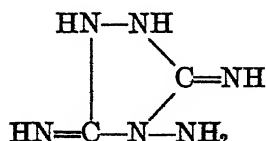
which on ring closure loses a molecule of aniline, to give the triazolone. The second substance, a sulfur-free base, was found (18) to be triphenylguanazole. Its formation by this reaction showed that the process was a general one for the preparation of triarylguanazoles:



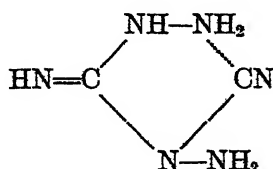
Pellizzari and Roncagliolio (104) examined the reaction of aminoguanidinium chloride with urea and found that 3-iminotriazolidene



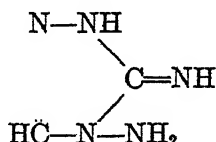
is formed. Pellizzari and Cantoni (100) found that chloro- and bromo-cyanogen react with hydrazine to form, besides diaminoguanidine, a cyclic derivative, which later investigation by Pellizzari (98) showed was a triazole derivative



the formation of which evidently proceeds through the formation of a cyanodiaminoguanidine

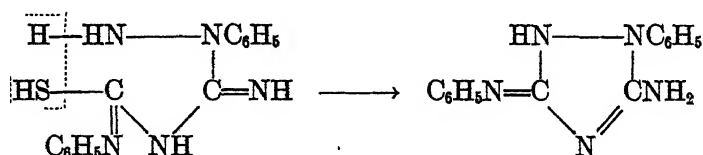


which undergoes ring closure by the intramolecular ammonation of the nitrile group. Gaiter (52) found that diaminoguanidine reacts with formic acid to yield a formyl derivative which, like the corresponding derivative of aminoguanidine, loses water to give 4-amino-3-iminotriazole

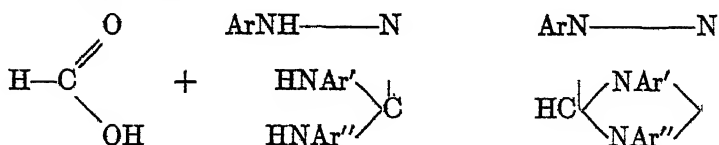


The reaction appears to be general, since with acetic acid the corresponding methylaminoiminotriazole is formed. The properties and derivatives of these substances were carefully studied by Gaiter (52).

Fromm and Göncz (46), Fromm and Vetter (49), Fromm and Weller (50), Fromm, Kayser, Briegleb, and Föhrenbach (48), Fromm, Bruck, Runkel, and Mayer (45), Fantl and Silbermann (37), and Arndt and Tschenschner (4) have very exhaustively examined the formation of triazoles from their (aminoguanido)arylthiureas. The mechanisms involving ring closure are quite complicated, and for details the original papers should be consulted. One example will suffice to illustrate the general mechanism involved. Phenyl(aminoguanido)phenylthiurea through the elimination of hydrogen sulfide forms 1-phenyl-3-anil-5-aminotriazole:

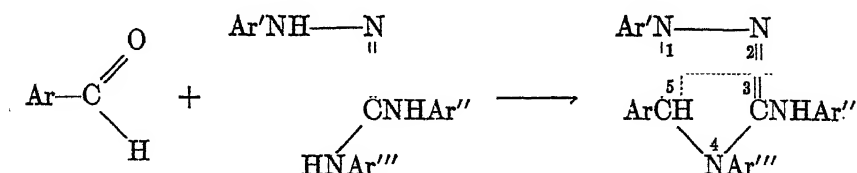


(c) *Nitron*. The "endoiminotriazoles" of Busch (14) are a series of triazole derivatives of practical interest to the analytical chemist. They are derived from aminoguanidine. The reactions are of further interest in that aminoguanidine appears to react in the symmetrical form only. Busch (14) found that triarylamino-guanidines condense with formic acid in the following manner:



The products are finely crystalline, mostly yellow, and possess strong basic properties. They are stable to acids, but are readily hydrolyzed to the original materials by alkalis. They form very insoluble nitrates. Busch and Mehrtens (17) also found that acids other than formic acid could not

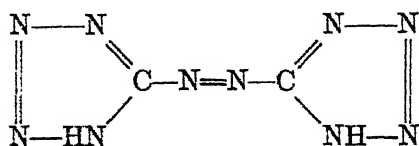
be used. If, however, phosphorus trichloride is added, the reaction proceeds smoothly, through the intermediate formation of the acid chloride. The structures of these compounds were demonstrated as follows (14). The triarylamino guanidines combine, without difficulty, with an equimolecular quantity of an aldehyde with loss of water, to form triazoles



The structures of the resulting 1,4,5-triaryl-3-arylamino dihydrotriazoles were readily indicated by acid hydrolysis. With oxidizing agents, the two labile hydrogens, one in the 5-position and the other on the amino group, are easily removed, with the formation of a nitrogen bridge between the 3- and the 5-carbon atoms, forming the "endoiminotriazole." The application of these substances to the gravimetric determination of nitric acid has been examined by Busch (15), Desvergues (32), and Heck and Mellon (62). Schmidt (127) has described the nitron-nitroform salt, Krauz and Turek (74) the trinitrobenzoate, and Lange (75) the difluophosphate.

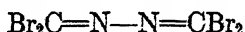
(d) *Tetrazoles*. The formation of the tetrazole ring by the isomerization of guanyl azide has been described, and the relation of aminotetrazole to other nitrous acid transformation products of aminoguanidine has been pointed out. It is of interest to recall that, although semicarbazide forms a similar azide, Thiele and Stange (163) found that it does not isomerize to a tetrazole ring, but yields, instead, hydrazoic acid. Thiele (147), the first to prepare aminotetrazole from aminoguanidine, has described many of its salts and organic derivatives. He was the first to demonstrate that the amino group is capable of diazotization and of coupling with aromatic amines. Thiele and Marais (159) studied the chemistry of diazotized aminotetrazole, "diazotetrazolic acid." It decomposed quantitatively on warming in aqueous solution and gave 1 mole of cyanogen and 5 molecules of nitrogen. By careful reduction, tetrazolyhydrazine was prepared and isolated as the benzal derivative, from which the free tetrazolyhydrazine was obtained as yellow crystalline pellets by hydrolysis. Thiele and Ingle (157) described other derivatives and other properties of aminotetrazole. The acid hydrolysis is of considerable interest. Aminotetrazole was found to be extremely stable; boiling for 5 hr. with fuming hydrochloric acid at 160°C. caused no decomposition, and hydrolysis did not take place until a temperature of 200°C. was reached. Hydrazine, nitrogen, ammonia, and carbon dioxide were

formed. Thiele (150) obtained azotetrazole by oxidation of aminotetrazole



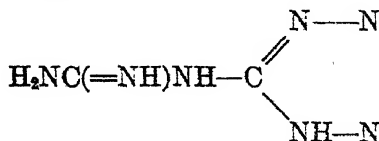
Azotetrazole

which was capable of reduction to a hydrazo derivative. On treatment of the hydrazotetrazole with bromine, an "isocyantetrabromide"



was obtained; it is volatile in steam, insoluble in water, and easily soluble in all organic solvents. Distillation in alkaline solution produced a substance believed to be a free halogenoid, $\text{OC}=\text{NN}=\text{CO}$, or its polymer. Treatment of the alkaline solution with zinc dust gave a substance, which from its hydrolysis products and odor, was thought to be "isocyan," $\text{C}=\text{N}-\text{N}=\text{C}$. Other derivatives of azotetrazole and hydrazotetrazole were described by Thiele (152).

In 1929 Stollé and Shick (144) found that an aqueous solution of hydrazoic acid reacts with dicyandiamide to form aminotetrazole. Using aminotetrazole prepared in this manner, Stollé (140) prepared a large number of new aminotetrazole derivatives, and gave detailed directions for each preparation. The mechanism given for the formation of aminotetrazole from hydrazoic acid and dicyandiamide is of interest here, since undoubtedly the precursor is the azide of aminobiguanide. This latter substance isomerized to guanylamino-tetrazole

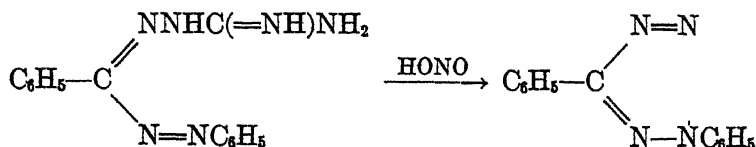


Guanylamino-tetrazole

The same compound may be prepared from cyanamide and aminotetrazole. Either product on heating at 200°C . yields ammonia, carbon dioxide, and aminotetrazole. A somewhat more simple mechanism may be postulated, in which the hydrazoic acid brings about a depolymerization of the dicyandiamide to cyanamide.

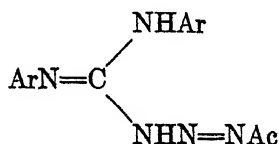
The guanazyls of Wedekind (165, 169, 170) have been described. From these Wedekind (166) found that, by treatment with nitrous acid, tetrazoles

were obtained. This is a new method for the preparation of aryl-substituted tetrazoles,



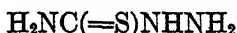
and may be regarded as a simultaneous oxidation, hydrolysis, and ring closure. The guanyl group forms water, nitrogen, and carbon dioxide. From the guanazylmethanes (170) similar tetrazoles were obtained, in which alkyl or carboxyl groups were substituted on the carbon atom of the ring. Wedekind (164, 167, 168) and Wedekind and Stauwe (171) have studied extensively the properties of these phenylated tetrazoles.

Busch and Bauer (16) attempted to prepare diazo derivatives of their diarylaminoguanidines

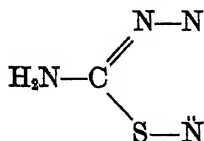


but found that they were immediately converted into tetrazoles, which from the structures of the starting material are *C*-(arylamino)aryltetrazoles.

It is interesting to point out that thiosemicarbazide,



in contrast to semicarbazide and aminoguanidine, forms no azide on reaction with nitrous acid. Freund and Schander (44) isolated a substance of the composition $\text{CH}_2\text{N}_4\text{S}$, which by its hydrolysis to cyanamide, sulfur, and nitrogen, was shown to have the constitution

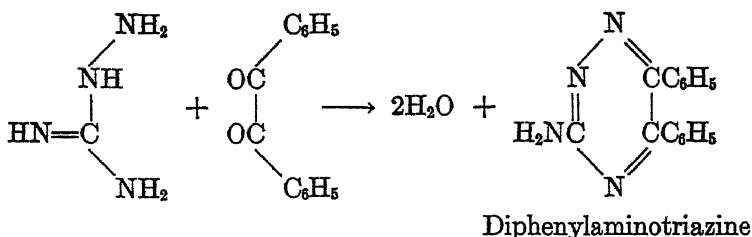


As the substance is an aminotriazole in which one of the ring nitrogens has been replaced by sulfur, it was called aminothiotriazole. (For completeness see the papers by Freund and Paradies (43) and Freund and Hempel (42).)

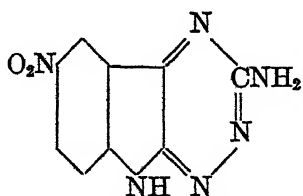
2. Six-membered rings

(a) *Asymmetric triazenes*. Thiele and Bihan found that aromatic α -diketones (154), as benzil and phenanthraquinone, reacted much less

readily with aminoguanidine to form aminotriazines than did the aliphatic α -diketones (155). The reaction of benzil with aminoguanidine proceeds as follows

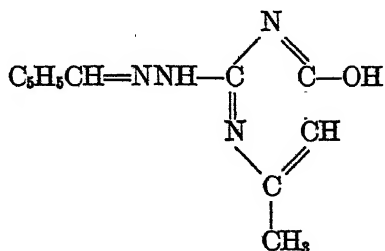


to form diphenylaminotriazine. Phenanthraquinone, under the same conditions, yields aminophenanthriazine. The aminotriazines are but very slightly basic and are unreactive towards nitrous acid. In 1927 De (27) prepared the corresponding compounds from acenaphthenequinone and β -naphthoquinone. Treatment of these compounds with concentrated potassium hydroxide replaces the amino group with a hydroxyl group. The hydroxy compounds are soluble in alcohol and give a solution of deep red color and greenish fluorescence. In a more recent paper, De and Dutta (29) showed that the aminotriazines derived from aminoguanidine are dyestuffs which color wool from yellow to a reddish brown. A number of new aminotriazines were prepared, in particular those of isatin. For example, 5-nitroisatin and aminoguanidine yield 3-amino-6-nitroindotriazine:

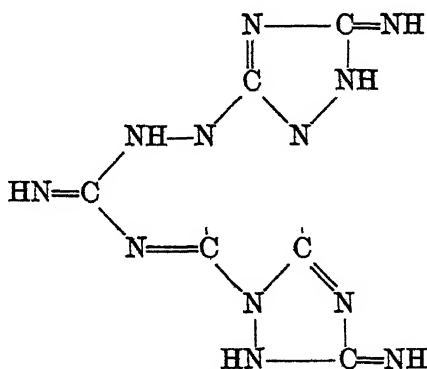


3-Amino-6-Nitroindotriazine

(b) *Pyrimidines*. With acetoacetic ester Thiele and Bihan (154) found that benzalaminoguanidine is transformed into a derivative of methylguanil:



were aminoguanidines and aminobiguanides. In 1911 Hofmann and Ehrhart (64) investigated the reaction of dicyandiamide and hydrazine hydrochloride in the solid state. By heating a mixture of dicyandiamide with dry hydrazine hydrochloride up to 280°C ., and extracting the product with hydrochloric acid, they obtained a white powder having the composition $\text{C}_6\text{H}_8\text{N}_{12}\cdot\text{HCl}$. They termed this "melamazine." In alkaline solution, air oxidizes melamazine to a bluish violet dye, which was isolated as a barium salt. In a subsequent paper Hofmann and Ehrhart (65) reported that the substance designated as melamazine contained only six instead of eight hydrogen atoms. They assigned the following structure to their compound:



Trisdesaminoguanazole

When dicyandiamide was heated on the water bath with its own weight of hydrazine hydrate, the air oxidation produced an intensely red material, which was believed to be due to a hydrotetrazine ring which is easily oxidized to a tetrazine ring. On continued heating until no more ammonia was evolved, the tetrazine, which was not isolated, disappeared, and guanazole was formed quantitatively. When this was heated to 270°C ., it lost ammonia and gave trisdesaminoguanazole. Melamazine is therefore a pyrolytic product of guanazole.

VI. USEFUL PROPERTIES OF AMINOGUANIDINE

Aminoguanidine and some of its derivatives are of practical importance, at least potentially, because of their properties as explosives and as physiological reagents. The explosive character of aminoguanidine derivatives was recognized by Thiele (147), and in recent years patents have been granted which relate to this property. Guanidine and its alkyl and aryl derivatives have been extensively investigated in regard to physiological properties, but, on the other hand, aminoguanidine and its derivatives have received very little attention.

A. Explosive properties of aminoguanidine

The explosive character of the reaction products of aminoguanidine with nitrous acid has been described (66, 67), and these derivatives are finding application in that field. This work has been reviewed by Stettbacher (136), Rinkenbach and Burton (120), Oddo (91), and Grottanelli (54). The general application of guanidine derivatives to explosives is also reviewed in a recent monograph by Stettbacher (135). A rather comprehensive patent on the use of these materials as explosives was obtained by Rathsburg (114) in 1921. An Australian patent (71) covers the use of guanyl azide picrate as an explosive. Hofmann, Hock, and Roth (69) describe the preparation of guanyl azide perchlorate from aminoguanidine, perchloric acid, and sodium nitrite. In comparison with Thiele's (147) guanyl azide nitrate, which is not detonated by rubbing or a blow, the perchlorate explodes violently.

B. Physiological behavior

Thiele (147), in his paper of 1892, evinced considerable interest concerning the physiological effects of his new compounds. Aminoguanidinium chloride was found to be a typical myo-poison. Its effect on the frog and toad was to cause a twitching of the fibrous muscles which lasted for many days. Benzalaminoguanidinium chloride was also reported to be a poison which, when present in the stomach or in the blood (100 mg. per kilogram of body weight in the blood), caused violent epileptic convulsions from which the test animals entirely recovered. The sodium salt of 5-aminotetrazole was found to be non-poisonous. Aqueous solutions of the free acid were observed to promote the growth of mouldy fungus.

Garino (53) has studied the comparative toxicity of guanidine and its amino derivatives. Guanidine is more toxic to infusoria and small crustacea than aminoguanidine, the latter more so than diaminoguanidine, and this in turn more toxic than triaminoguanidine. Eggs of *Strongylocentrotus* placed in a 0.04 *N* solution of guanidine are arrested in the morula stage; in aminoguanidine they are arrested in the blastula stage; while in triaminoguanidine they develop to the stomite stage. Similar effects were observed on the germination of lentil seeds. Experiments on guinea pigs likewise showed that, as the number of amino groups increases, the toxicity of guanidine diminishes.

A more comprehensive study of the comparative physiological action of guanidine and its amino, alkyl, and aryl derivatives has been made by Alles (1). In general, the blood pressure response consists in a fall of the blood pressure followed by a rise that may be quite prolonged. The intensity of the effect of guanidine derivatives varies; acetyl-, methyl-,

dimethyl-, ethyl-, and ethanol-guanidines have a much more marked effect than guanidine or aminoguanidine. The heart rate and amplitude of the heart beat are affected considerably, the effect being most marked with ethyl- and dimethyl-guanidines, while aminoguanidine has a less marked effect on the heart rate and amplitude of the heart beat; guanidine has no appreciable effect. The aryl derivatives of guanidine, such as *s*-diphenylguanidine and triphenylguanidine, are active in small doses, causing a fall in blood pressure and a decrease in the heart rate, the former derivative being very active in this respect. The respiratory effect is most marked with acetylguanidine. While the alkylguanidines and aminoguanidine all have considerable effect on both the respiratory rate and amplitude, the aryl derivatives are not marked in their action. The general effect of guanidine is paralysis, occasional convulsions, dyspnea, and prostration. Lettes has studied the effect of aminoguanidine on hemoclastic crisis (76) and on the blood picture (77). Aminoguanidine produces a blood picture similar to pernicious anemia. Nielsen and Widmark (90) have determined the effect of aminoguanidine on the excretion of uric acid in rats; they found no increased effect.

Certain substituted guanidines have been investigated in order to find pure substances possessing an action similar to that of insulin. A review of proposed insulin substitutes has been given by Braun (11) and by Braun, Mason, and Brown (12). Most of these compounds contain a guanidine and an amino group or two guanidine nuclei (39, 40). Conard and Shriner (20) investigated the condensation products of aminoguanidine with *p*-dimethylaminobenzaldehyde for insulin-like activity, but found no effect.

VII. SUMMARY AND CONCLUSIONS

A review has been given of the chemistry of aminoguanidine and related compounds.

1. Aminoguanidines may be synthesized by methods involving reduction of nitro- and nitroso-guanidines and by hydrazination and hydrazinolysis of compounds related to guanidine, or by a combination of these latter processes.

2. The hydrolysis of aminoguanidine in acid or basic media proceeds in simple step-wise fashion to semicarbazide and hydrazine. In contrast to semicarbazide, aminoguanidine is extremely resistant to acid hydrolysis.

3. Attempts to isolate free aminoguanidine result in the formation of *s*-diaminotetrazine. The mechanism for its formation and its relation to the simpler hydrolytic products of aminoguanidine is not clear.

4. The oxidation of aminoguanidine has been studied to only a limited extent. Permanganate ion in acid solutions yields azodicarbamide, and

hydrolysis of this compound yields unstable "diimide," which could not be isolated.

5. The reaction with carbonyl compounds leads to well-defined guanylhydrazones, but only nitroaminoguanidine has been systematically applied to analytical organic chemistry.

6. The chemistry of the reaction of aminoguanidine with nitrous acid has been reviewed and correlated. The products obtained depend upon the conditions of the reaction media.

7. Syntheses starting from aminoguanidine lead to the formation of nitrogen chains containing three, four, six, and seven nitrogen atoms of *exceptional* stability. Their inclusion in the family of hydronitrogens must lead to some revision of the comparative stability of nitrogen chains.

8. Penta-, hexa-, and condensed heterocyclic ring compounds containing two, three, four, and five nitrogen atoms in the ring have been synthesized from aminoguanidine and its derivatives. The contribution of aminotriazoles and tetrazoles to diazotizability in non-aromatic systems has been reviewed.

9. The properties of aminoguanidine and its derivatives as explosives have been pointed out.

10. The known physiological properties of aminoguanidine have been reviewed and a comparison made with the alkyl and aryl derivatives of guanidine.

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THE COLOR OF ORGANIC SUBSTANCES

GILBERT N. LEWIS AND MELVIN CALVIN

Department of Chemistry, University of California, Berkeley, California

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The absorption of light by organic molecules has been the subject of an enormous amount of successful experimentation, and yet very few fundamental principles have been discovered, as may be seen in the numerous reviews that have been published (40, 46, 57, 60, 71). The connection between the finer structure of absorption bands and the known bands of atomic vibration is being very satisfactorily established, but the position and intensity of the main electronic absorption bands can rarely be predicted. Yet the prediction of these bands, and thence the color, from the structure of the molecule, should be one of the chief goals of chemistry.

Despite the great importance of dyes, which absorb intensively in the region of visible light, exact and systematic data are at present available chiefly for the relatively simple organic substances that absorb in the ultraviolet only. Because of the great success in the interpretation of the spectra of atoms and diatomic molecules, it has been natural to study first the simpler molecules. Moreover, to the simpler molecules quantum mechanics may be applied by methods of approximation which are not excessively arduous and which represent a reasonable extrapolation from the known into the unknown. Recently numerous attempts have been made to extend the quantum-mechanical methods (20, 33, 49, 65) to molecules of some complexity, such as benzene and butadiene.

Such studies will undoubtedly continue to be prosecuted and may lead to the discovery of generalizations applicable to even more complex molecules. But it appears unlikely that in the near future these means alone will permit the interpretation of the absorption of light by such complex structures as the organic dyes.

For this reason it has seemed to us that it might be useful to reexamine the data of light absorption and to see whether, by applying the more inductive methods of chemistry, together with such general results of quantum theory as are applicable to all systems, we may obtain a better understanding of the data. Starting with the idea that in the absorption of light the energy is taken up by electronic oscillations, we have considered these oscillations as analogous to classical oscillations, but subjected

to the rules of simple quantization. As we have tested this quasi-classical model with the various known facts relating to light absorption, we have found that it affords in many cases a qualitative, and in a very few cases a quantitative, interpretation of the experimental facts.

When we consider a heavy diatomic molecule such as I_2 , we speak of the rotation and vibration with the feeling that these words, and the implied analogy to rotations and vibrations of large objects, will be useful in the understanding of the properties of such a diatomic molecule. When we apply similar words and analogies to a molecule composed of light atoms such as H_2 , it is realized that the picture is a less adequate one, and when we proceed to the very light particles, the electrons, the analogy has not even been attempted. It is, however, to be noted that it is not the mass alone that determines the degree of approximation to the classical picture. Hydrogen held to another atom by a very loose bond may undergo motions nearer to the classical than iodine held by a strong bond. So if even so light a particle as the electron is in a field of small constraints, the various electronic excitations may be called vibrations. We shall therefore attempt to interpret the absorption of light by dyes, and even by substances which have only ultraviolet bands, in terms of such a quasi-classical model; and thus consider the molecules as containing vibrating electronic systems, which are subject to the rules of quantization applicable to an oscillator. We must consider not only the various possible modes of vibration and the laws governing them, but also the interaction between electronic and atomic vibrations in the molecule.

Our first task must be to attempt a simplification of the complex band system that is found in many dyes. Even the individual broad electronic bands frequently show a finer structure, which has successfully been attributed to atomic vibrations associated with electronic transitions. This structure may be accentuated by various means. One method is to work at low temperatures where the initial vibrational state of all of the molecules is at the same (or nearly the same) energy. Figure 1 shows the absorption of dodecapentaenic acid (25) in a mixture of ether and alcohol, at room temperature (above) and at liquid air temperature (below). We shall see later that the more pronounced structure in the second case, while it may be partly due to lower temperature, is probably chiefly attributable to a change in the physical character of the solvent.

Even when a broad band is resolvable into narrower bands, the latter often have half-widths of several hundred Ångström units. As far as existing experimental material goes, this may be explained in either of two ways. One explanation is that, in addition to atomic vibrations of high energy, such as are brought out in figure 1, there are in a complex molecule

many types of vibration (and rotation) of much smaller energy. It may therefore be that the narrow bands are themselves resolvable into still narrower ones. The other explanation also assumes these vibrations of small energy, but assumes that the main excitation is to one of the widely spaced energy levels, and that the energy is almost immediately transmitted to the vibrations of smaller energy. If this process is so nearly instantaneous that the mean life in the initial excited state is only of the order of 10^{-13} to 10^{-14} sec., the "natural" broadening would account for the observed widths of the bands.

Even if the band structure due to atomic vibrations is absent or has been accounted for, the system of electronic bands of a colored substance is often bewilderingly complex. In some dyes the multiplicity of electronic bands is due to the fact that the dyes are mixtures. Even if the dye is carefully purified it may be subject to reversible changes in composition; thus an indicator molecule may add or lose hydrogen ion, or other acid,

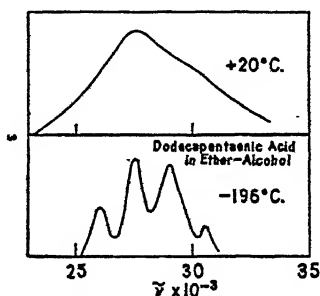


FIG. 1. Absorption curves of dodecapentaenic acid in a mixture of ether and alcohol¹

in one or more stages. In rarer cases, such as trinitrobenzene, the indicator may add a base.

One of the first careful analyses of the spectrum of an indicator was carried out in this laboratory by Adams and Rosenstein (1), who were able to obtain the curve for the molar extinction coefficient of each of the ions that are present in aqueous solutions of crystal violet. These curves are reproduced in figure 2. The central band is due to the simple ion; that on the left is due to the addition of one hydrogen ion, and that on the right to the addition of two hydrogen ions.

Moreover, the solvent, especially if it is a substance like water, may

¹ All of the figures used in this paper have been redrawn. Clerical assistance of the Works Progress Administration (OP-465-03-3-147) is gratefully acknowledged. In all of the figures the molar extinction coefficient, ϵ , or some function thereof, is plotted as ordinate; as abscissa the wave number $\bar{\nu}$ (in cm^{-1}). The extinction coefficient, if in arbitrary units, is designated by α .

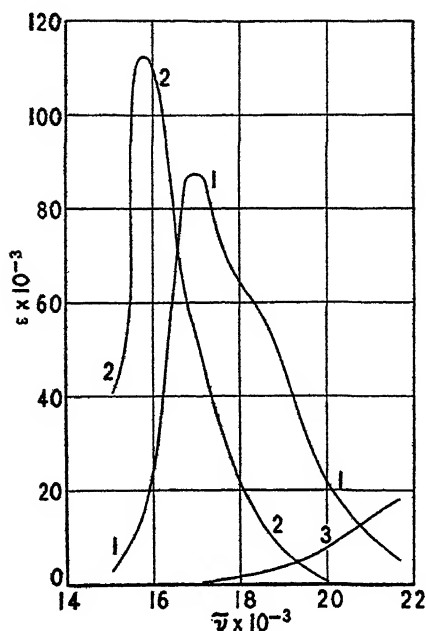


FIG. 2. Absorption curves of the several ions of crystal violet in water

Curve 1, absorption curve for $[((\text{CH}_3)_2\text{NC}_6\text{H}_4)_3\text{C}]^+$

Curve 2, absorption curve for $[((\text{CH}_3)_2\text{NC}_6\text{H}_4)_2((\text{CH}_3)_2\text{NHC}_6\text{H}_4)\text{C}]^{++}$

Curve 3, absorption curve for $[((\text{CH}_3)_2\text{NC}_6\text{H}_4)((\text{CH}_3)_2\text{NHC}_6\text{H}_4)_2\text{C}]^{+++}$

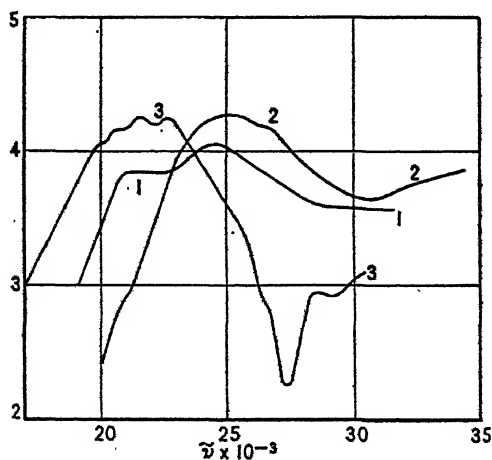
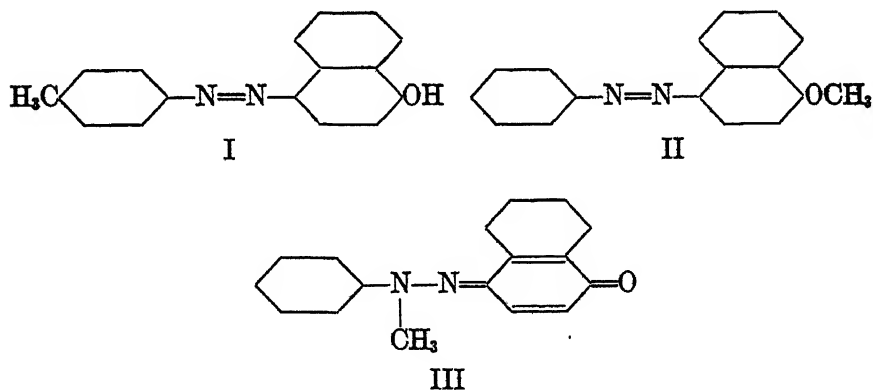


FIG. 3. Curve 1, absorption curve of *p*-methylbenzeneazo- α -naphthol; curve 2, absorption curve of benzeneazo- α -naphthol methyl ether; curve 3, absorption curve of naphthoquinone *N*-methylphenylhydrazone. The solvent in each case was benzene.

combine with the colored solute to produce a number of definite molecules, each of which has its own absorption. These compounds are ordinarily the result of a hydrogen bond between solvent and solute, but sometimes aromatic solvents like benzene form compounds with aromatic solutes, especially those containing the nitro group, when another type of resonance binding is manifest. It is our belief that all pronounced changes in color, when passing from one solvent to another, are due to such definite solvates, except in the single type of substance exemplified by *p*-nitroaniline, which we shall discuss later. The colored solute may combine with itself to form polymers which have their own characteristic absorptions, as we shall later illustrate.

If the solute is capable of tautomerism this may give rise to a complex spectrum, as illustrated by the work of Shingu (64) on a substance, one of whose tautomeric states is expressed by formula I, the other state being produced when the hydrogen is transferred from oxygen to nitrogen. Its complex absorption curve, curve 1 of figure 3, is due to these two substances, as was demonstrated by the author when he prepared the two corresponding methyl derivatives II and III, which give rise to the simpler curves 2 and 3 of the same figure.



Geometrical tautomerism also gives rise to mixed spectra, as, for example, in the azo dyes. Brode (6) found in benzeneazophenol two band systems which he suggested might be due to two modifications. Now a similar pair of band sets can be found in all azo compounds and, since the discovery of *cis-trans* isomerism (21) in such substances, they can definitely be ascribed to the *cis*- and *trans*-forms. In the case of stilbene the *cis*- and *trans*-forms have long been known, each in the pure state, and the two absorption curves (67) are given in figure 19.

When all pains have been taken to prepare a substance in a single

molecular form, and solvates are largely eliminated by the use of such a solvent as hexane, we still frequently find in an absorption spectrum, taken through the visible and well into the ultraviolet a number of separate electronic bands.

We shall attempt to classify these bands as (*A*) fundamental bands, or bands of electronic oscillation within the molecule as a whole, and (*B*) bands of partial or localized oscillation. The fundamental *A* bands may be further subdivided as follows: (1) Fundamental bands of the first order, that is, bands due to a transition to the first excited state. These are further classified as (*a*) a single band (*x* band) corresponding to oscillation in a single direction, (*b*) two bands (*x* and *y* bands) due to two mutually perpendicular oscillations, and (*c*) three bands (*x*, *y*, and *z* bands) which are to be found only in molecules in which the conjugating system has considerable extension in three dimensions. (2) Fundamental bands of the second order, due to a transition from the zero state to the second excited state of the fundamental oscillator.

As we proceed we shall attempt to justify this classification and to give examples of each of the enumerated types.

ABSORPTION AND TYPES OF BOND STRUCTURE

According to the original theory of Witt (70) a colored substance must contain one or more unsaturated groups, such as the vinyl or carbonyl groups, which he called *chromophores*. He also spoke of *auxochromes*, which are groups that greatly enhance the color of a chromophoric substance.

Even a substituent that is not ordinarily regarded as an auxochrome may have a decided influence upon the position and intensity of absorption bands. Figure 4 (31, 58) shows the absorption curves of acetone and hexaethylacetone. Although the effect of the substituent groups is a large one, it appears to be the result of shifting and modifying the acetone curve, without introducing any new electronic band. The influence of the substituents may be said to be one of induction, which may be regarded as a perturbation in existing electronic paths without altering their essential character.

On the other hand, the effect of an auxochrome, which will be illustrated in numerous figures, may be described as providing, through resonance, entirely new electronic paths. Such a substituent causes, as we shall see, not only a shifting of old bands, but the appearance of entirely new electronic bands. These new bands we are going to consider as due to oscillations within the molecule as a whole, or, as Rădulescu (56) has put it, of the "résonateurs d'ensemble."

Auxochromes, as pointed out by Wizinger (71), are of two kinds, which

he calls positive and negative. The first kind, which we shall call basic auxochromes, is typified by the NR_2 group, which may enter into resonance by using its lone pair of electrons to form a double bond with the adjacent atom (37). The other kind, which we shall call acid auxochromes, is typified by the NO_2 group, which may enter into resonance through the formation of a double bond by means of a pair of electrons which is contributed by the adjacent atom. The important connection between color and resonance was first pointed out by Bury (10). Before proceeding further with the problem of color we must first consider simple structures, which absorb chiefly in the ultraviolet.

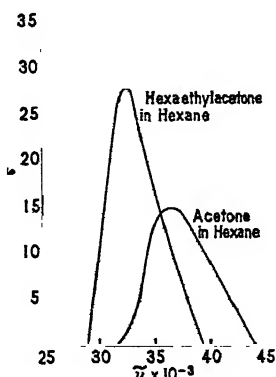


FIG. 4. Absorption curves of acetone and hexaethylacetone

The single bond

Molecules of the type called saturated do not ordinarily absorb light except in the extreme ultraviolet. It is true that methyl iodide absorbs down to 2700 \AA. , but, since this is approximately the absorption region of iodide ion, the absorption is probably to be attributed to the polarizability of the iodine itself. However, in the majority of organic molecules we shall be able to regard the bond as the seat of that mechanism which is responsible for the absorption of light, with occasional mention of the effect of non-bonding electron-pairs such as exist in the iodine atom. In our last section we shall consider systems containing odd electrons.

If we examine ethane, whose absorption spectrum is shown in figure 6, we see a continuous band beginning at about $62,000 \text{ cm}^{-1}$. The lack of any structure, and the steady increase in intensity of absorption with increasing frequency, indicate either that the electronic excitation and the photodissociation of the molecule occur as a single act, or that the dissociation follows the electronic excitation after a very brief period of time. We do not know whether the first absorption is in the C—C bond or the C—H

bond. Presumably the two absorptions occur in very nearly the same region. We may assume then, for purposes of illustration, that the C—C bond begins to absorb at about $62,000\text{ cm}^{-1}$

Let us begin now to develop our fundamental idea of the electronic excitation by light, realizing that while the cases that we must present first are the simplest of all, they are, on the other hand, the farthest removed from the conditions that best justify the employment of the quasi-classical method that we are adopting.

Let us assume that the pair of electrons in the C—C bond constitutes an oscillating unit, and think of its motion along the line joining the two carbon atoms. The electronic vibrations that we are going to consider are so rapid compared with atomic motions that we may regard the electrons as moving in a fixed frame of atoms. If, when the electron-pair is displaced from its equilibrium position, the restoring force is approximately proportional to the displacement, the potential is proportional to the square of the displacement, and we shall have a potential curve in the form of a parabola similar to those that we have drawn in figures 5 and 10. If we regard the electron-pair as a single unit, application of quantum mechanics leads to the familiar set of energy levels, $v = 0, 1, 2 \dots$, and we shall suppose that the value of $h\nu$ corresponding to light absorption is the difference in energy between $v = 0$ and $v = 1$.

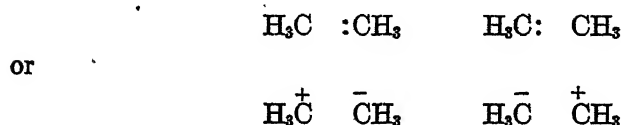
One of the striking consequences of this point of view is that we are led to consider a *zero-point energy* of electronic vibration, corresponding entirely to the familiar zero-point energy of atomic vibration. Whether the consideration of this zero-point energy of the electrons will prove serviceable in this extreme case of the single C—C bond is perhaps doubtful, but we hope that it will become useful in dealing with the relation between the optical properties and the resonance energy of more complex chromophores.

We shall discuss frequently the correlation between color and chemical resonance. This phenomenon of resonance has often been given an interpretation which has never been found at variance with our chemical knowledge, and which may be stated as follows: A substance to which only one reasonable formula can be assigned has properties in accord with that formula. When to a substance two or more structures might be assigned, such that one may be derived from another merely by the shifting of electron-pairs, these structures are said to be in resonance with one another, especially if the energies corresponding to the several structures, as well as the relative positions of the atoms, are not widely different. Such a resonating substance is to be regarded not as a mixture of various molecules corresponding to the various structures, but rather as having a single kind of molecule which, however, partakes of the character of the

several contributing structures. Thus, for example, in different reactions it may behave in the various ways characteristic of the individual structures.

While we assign to a resonating molecule only a single set of properties, yet we must recognize that even in its state of lowest energy the molecule cannot be regarded as a set of atoms and electrons occupying fixed positions. The idea of zero-point energy, or the related principle of uncertainty of Heisenberg, leads to the consideration of some sort of flux which in its various phases may approach closely to some one of the electronic structures that are said to contribute to the resonance.

This concept, of which we shall make extensive use, may now be illustrated in its simplest, but perhaps least important, application. Considering the molecule $\text{H}_3\text{C}-\text{CH}_3$ we may write the two additional formulas that contribute to resonance in the single C—C bond, namely,



Now the contribution of these two forms to the actual state of the molecule is small; nevertheless, it is this very possibility of alternation of phase in the direction of the one form or the other, involving displacement of electric charge, that must be held responsible for the ability to absorb light. We need, however, devote no more attention to this simple type of resonance, since we have many more important types of resonance to discuss.

The double bond

When we come to the double bond, which is the most important unit in the mechanism of light absorption, we must differ at the outset from a conception that has been frequently advocated in recent years and is now generally accepted. According to this conception the electron-pairs of a double bond are different, one pair being designated as σ electrons and the other as π electrons. There is no objection, as a basis of some mathematical approximation, to the fiction that one pair still has the characteristics of a single bond while the other is loosely bound and is responsible for the phenomena of resonance and color. However, to the chemist who has not forgotten the brilliant strain theory of Baeyer, the two bonds of ethylene must be regarded as identical, and differing in degree, but not in kind, from the bonds of other ring systems. Without mentioning numerous facts of chemical behavior, it will be sufficient for our present purpose to point out that, even with respect to the absorption of light, the cyclopropyl group, in which all the electron pairs would certainly be regarded as σ electrons, is a chromophore of the same type as the ethylene

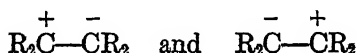
group, although less powerful. Thus Carr and Burt (12) have shown that in several types of compounds the absorption spectra of those compounds with a three-membered ring are intermediate between those with the double bond and those with ordinary single bonds.

When we ascribe the chromophoric character of ethylene to two electron-pairs held conjointly and symmetrically between the two carbon atoms, we already have a system which is far beyond the present powers of exact quantum mechanics. We are therefore forced at the outset to adopt some semi-empirical method.

As examples of double-bonded structure we may take the following types:



In the first compound, the formula, as written, is the major contributing structure, and the two symmetrical minor contributing structures are the ionic forms,



So may be written the corresponding contributors in the other cases. It will be noted that while there is no dipole moment in the first and fourth cases, because of symmetry, in the second, third, and fifth cases the molecule will have a dipole moment. This, however, is of only indirect concern to the problem of color, for we shall see that it is not the dipole moment but the polarizability that is of immediate importance.

Simple substances of the ethylenic type begin to absorb at 2000 Å., those containing the carbonyl group have a first absorption maximum at about 2800 Å., while azomethane, $H_3CN=NCH_3$, is yellow and has its first absorption maximum at 3500 Å. We have not found data for simple compounds containing the double bond between carbon and nitrogen or carbon and sulfur, but the former will presumably lie between the ethylene and the carbonyl, and the latter will be found to absorb at longer wave lengths than azomethane. We do not know what part the lone or non-bonding pairs of electrons on nitrogen, oxygen, and sulfur may take in the process of light absorption, but shall assume that it is not an important one.

What is it that determines the difference in the chromophoric character of these groups? If we assume that the double bond acts as a single oscillating unit, we may consider that the restoring force, for unit displacement of electrons in the line joining the atoms, diminishes in the above series from $C=C$ to $C=S$. In other words, if we plot the potential against the displacement we shall have a series of parabolas (figure 5), of which the height at a given value of the displacement is proportional to k , the constant of restoring force. Using the formula which will be developed in the next

section, we have obtained the relative values of k in the case of the three bonds for which we have just given the absorption maxima.

Even if we are justified in drawing such curves, we do not know whether they would remain parabolas for any large displacement. Nevertheless, it is evident that a continued displacement of this character would lead eventually to a condition corresponding to one of our formulas, which we have called the ionic contributors to resonance. Therefore we may expect that these polarized forms will contribute more to the actual state of resonance the lower the value of k .

Since the amount of the relative contribution to resonance of the major and minor forms depends upon the difference in energy, we may make the contribution of the minor forms greater by diminishing their energy or by

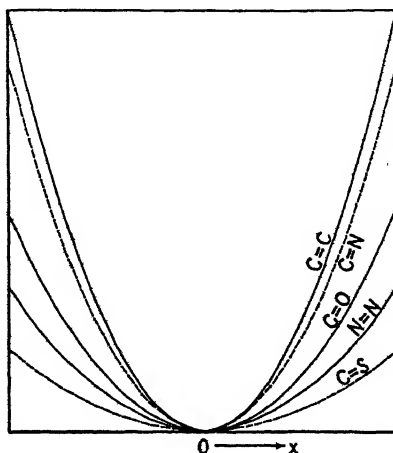


FIG. 5. Potential curves for different chromophores

increasing the energy of the major or classical form. We shall find it convenient in one of the following sections to ascribe the difference between the several double bonds to differences in double bond strain in the classical structure. In other words, we shall say that there is an increasing strain in the double bond as we pass in our series from $C=C$ to $C=S$.

We have not found it necessary in tracing the relationship between optical properties and resonance to assume the kind of resonance that Pauling (50) and others have employed, in which the two electrons of an electron pair are separated while their spins are kept anti-parallel. In the first place such a resonance would not be directly related to the absorption of light and in the second place we believe that, whenever there is a strong tendency for such a process to occur, the pair is likely to break, to form an electromeric odd molecule such as the biradicals, which have been very fully studied by Müller (48).

Conjugation

The great class of organic dyes chiefly comprises substances whose color is due, not to single chromophores of the type we have been discussing, but to several such groups in a state of mutual conjugation. Usually we find an unbroken succession of alternating single and double bonds, either in single order or branching (cross conjugation). Diltney (18) made this statement more general by including any succession of atoms each of which is "coördinatively unsaturated." By this expression he meant to include

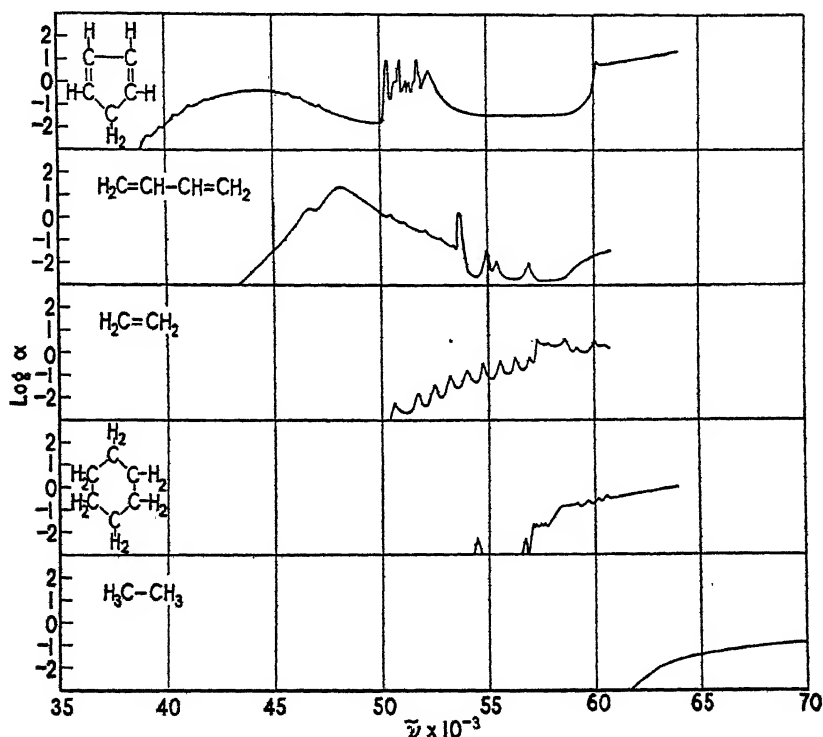


FIG. 6. Absorption curves of cyclopentadiene, 1,3-butadiene, ethylene, cyclohexane, and ethane

not only carbon atoms, each of which is attached to a double bond, but also atoms like nitrogen, oxygen, and sulfur, which are capable of forming "onium" compounds. There seems little doubt that in many of the important sulfur dyes there are chains of at least two sulfur atoms which join chromophoric groups into a single chromophoric unit. Even this definition is not quite broad enough, for it would not include the derivatives of cyclopropane, whose absorption spectra we have already discussed. Instead of attempting to complete such a formal definition, let us rather

investigate the nature of the effect produced by conjugation upon the absorption of light.

The simplest kind of conjugation is that between two double bonds in a symmetrical molecule such as butadiene or cyclopentadiene. The absorption curves of these substances, as well as those of ethylene, cyclohexane, and ethane are reproduced in figure 6 from the work of Scheibe and Grieneisen (61). The ordinate is $\log \alpha$, where α is a quantity proportional to the extinction coefficient, but expressed in arbitrary units. The two lowest

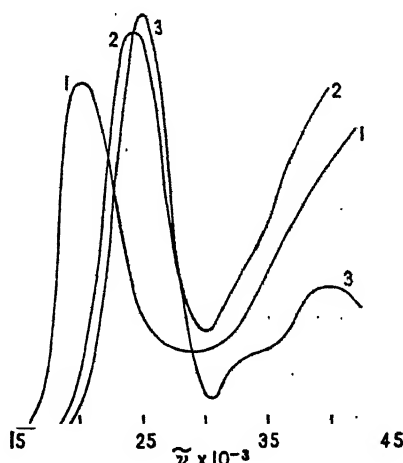
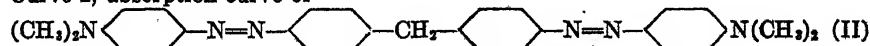


FIG. 7. Absorption curves of some azo dyes in ethanol

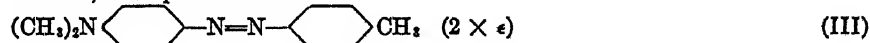
Curve 1, absorption curve of



Curve 2, absorption curve of



Curve 3, absorption curve of



curves show the type of absorption in single-bonded systems. The third is characteristic of a simple double bond, which already has in a considerable degree the properties of resonance. The two upper curves typify the absorption of conjugated systems. In these, and especially in the curve for cyclopentadiene, we have, in addition to an absorption suggesting that of ethylene, a new wide curve which we shall now attribute to electronic oscillation throughout the conjugating system. It is what we shall call a fundamental band. If we have a molecule with two single bonds

between the two double bonds, according to the scheme $C=C-C-C=C$, as in 1,4-pentadiene, we no longer have this fundamental band and the absorption is now that of isolated double bonds acting individually.

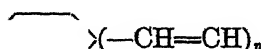
A CH_2 group placed between two parts of a conjugating system may be likened to an insulator introduced into an electrically conducting system, dividing it into two parts. Let us illustrate this in a more complicated case from one of the papers of Brode (53) on the azo dyes. In figure 7 the first curve is that for the fully conjugated structure (I), the second is for structure II, with a central "insulation," and the third shows double the molar extinction coefficient for substance III, which represents about one-half of one of the previous structures. It is evident that each half of substance II is absorbing nearly as though the other half were absent.

When a conjugated system is absorbing in its fundamental band it appears as though the individual oscillators have lost their individuality and have become subject to certain rules governing the whole molecule. We assume that these rules have to do with relationships in phase between the motions of the several oscillators. Before proceeding with a discussion of conjugation in general, we shall develop our concepts by dealing first with certain simple types of conjugated systems.

NEARLY LINEAR MOLECULES

As the simplest and best example of our ideas of conjugation let us consider in some detail the optical behavior of a long chain of alternating single and double carbon bonds, basing our discussion very largely upon the extremely important series of experiments carried out by Hausser, Kuhn and Smakula (23 to 29). The observations were made upon a series of diphenylpolyenes, upon polyenes with other end members, such as aldehyde, acid, and furyl groups, and upon various carotinoids. While all polyenic chains have a zigzag character, nevertheless they are non-branching chains which for our present purposes we may regard as linear.

Figure 8 shows the absorption in the visible and near ultraviolet of the compounds



Each curve represents a single electronic band, the structure being satisfactorily ascribed by the authors to the atomic vibrations characteristic of the olefins. This structure has been accentuated by the use of a solution in mixed ether and alcohol at -196°C . The same bands, but with the structure nearly eliminated, are obtained in solvents at room temperatures, as we have seen in figure 2. The steady increase in wave length with increasing length of the molecule is very striking. Moreover Hausser (23) has shown that, when the frequency of the first maximum is plotted against

the total number of conjugated double bonds for about seventy compounds of polyenic type, all of the points approximate to the same curve (figure 9).

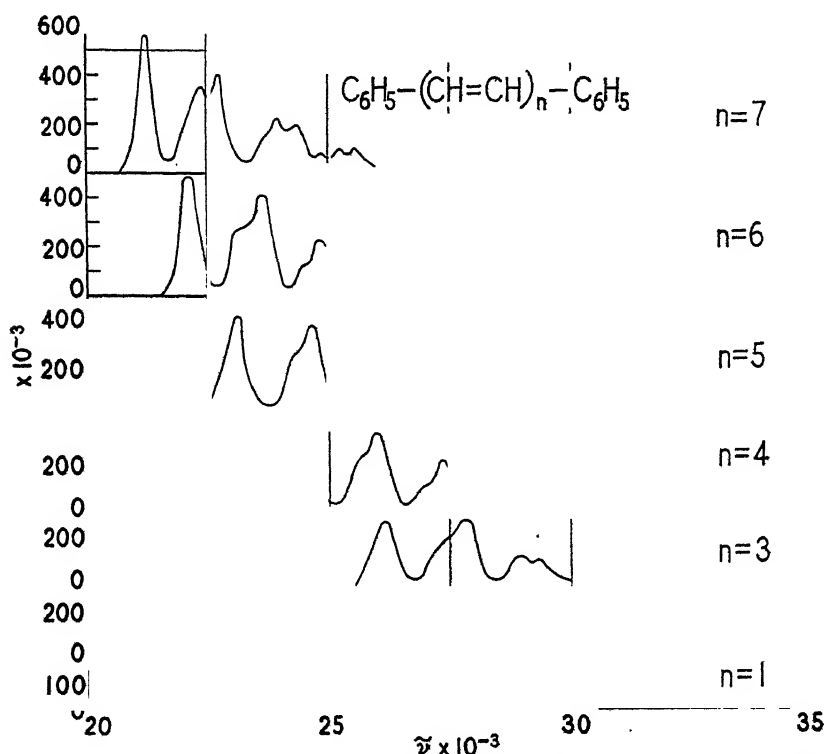


FIG. 8. Absorption curves in the visible and near ultraviolet of diphenylpolyenes in ether-alcohol mixtures at -196°C .

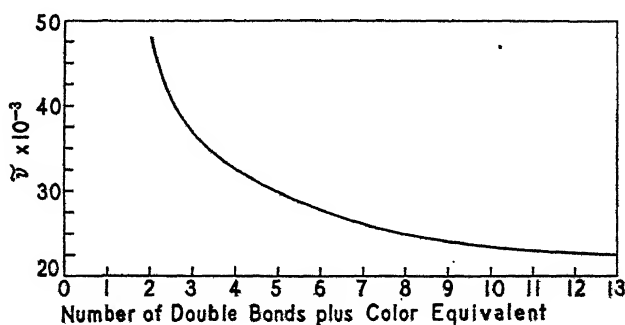
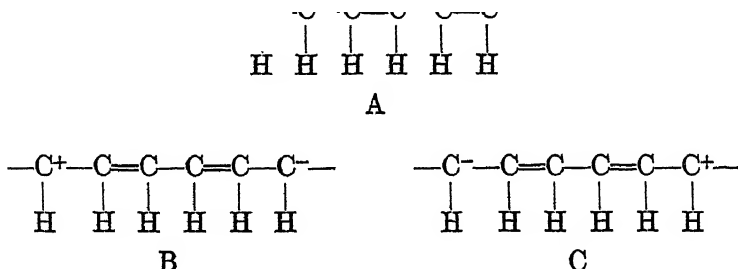


FIG. 9. Plot of frequency of first maximum against the total number of conjugated double bonds for seventy compounds of the polyenic type.

He includes all the double bonds in the end members except in the case of the phenyl group, to which he arbitrarily assigns a "color equivalent" of

one and one-half double bonds. His curve shows a simple functional relationship between the frequency of absorption and the length of the conjugated chain. What this relationship is we shall now attempt to ascertain.

Let us write for a polyene, omitting the end members, the major contributing structure A and the two symmetrical minor structures B and C:



We need not assume that the resonating molecule ever reaches the extreme forms B and C but rather that there may be concerted motions of the electrons from the major structure A, in the direction either of B or of C.

On account of its symmetry the normal state of the molecule has no dipole moment. If, however, it is placed in an electric field, for example, a positive plate at the right and a negative plate at the left, the electrons are shifted in the direction of structure B. The dipole moment produced per unit field strength is the polarizability. We may now consider this electronic displacement in either of two equivalent ways. We may consider the molecule as a whole and the total displacement from one end to the other, or we may consider the individual units ($\text{---C}=\text{C}$) and, ignoring



end effects, add the dipole moments produced in the several units. Let us choose the latter course. If μ is the moment produced in each unit in a field of strength E , then α , the polarizability, is given by the equation

$$\alpha = \mu/E \quad (1)$$

We do not need to decide how many electrons are involved in our process. If $-e$ is the effective charge which is displaced and x is the displacement from the normal position, then

$$\mu = ex \quad (2)$$

The electric force is $-eE$. When a displacement has taken place, this must be balanced by a restoring force which, assuming Hooke's law, may be written as $-kx$. Then

$$-eE = kx \quad (3)$$

Combining these equations we find for the coefficient of restoring force k the equation

$$k = e^2/\alpha \quad (4)$$

When our molecule is in an alternating electromagnetic field, such as that of radiation of wave length large compared with the dimensions of the molecule, we shall have an induced oscillation throughout the length of the molecule in which the displacement will be the same in magnitude and in direction for each unit. We are now going to assume that in the electronically excited states there are oscillations within the molecule that are of the same character as these induced oscillations. Let m be the mass of the effec-

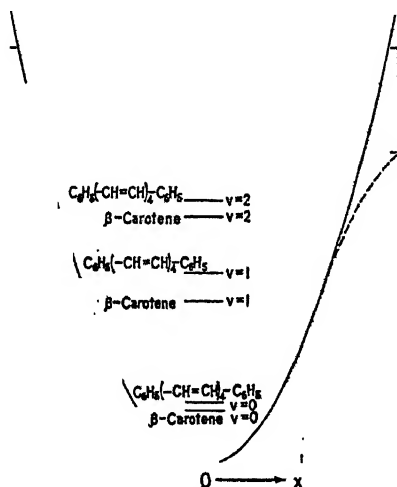


FIG. 10. Plot of potential against x , the electronic displacement

tive electrons in each unit, so that $-e/m$ is the familiar ratio of charge to mass for one electron; then in the molecule composed of n units the oscillations will be those corresponding to the constant k and to a mass equal to nm .

In other words, we have replaced our system of unit oscillators by a single oscillator with the same coefficient of restoring force, and with a mass proportional to the number of units. We may now use the ordinary methods applied to a simple linear oscillator. If we plot in figure 10 the potential against x , the electronic displacement, we obtain the parabola characteristic of simple harmonic motion, in which the potential is equal to kx^2 . We shall later consider a possible anharmonicity of the type represented by the dotted line.

The energy levels, W_v , of an oscillator of mass nm and restoring force constant k , are given by the expression

$$W_v = (v + \frac{1}{2})h\nu_0 \quad (5)$$

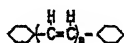
where $2\pi\nu_0 = \sqrt{k/nm}$ and v is the quantum number of the oscillation. Therefore the frequency of light which can change the oscillator from $v = 0$ to $v = 1$ is simply $\nu = \nu_0$. Changing to wave length λ , and using a new constant which includes the effective mass of one unit, we have the equation

$$\lambda^2 = k'n \quad (6)$$

20

15

10



2 3 4 5 6 7

FIG. 11. Plot of the square of the wave length against the number of units of the polyenic chain

Let us test this equation by means of the most extensive and accurate single series of measurements that have so far been obtained in the study of the absorption spectra of organic molecules. These are the measurements of Hausser, R. Kuhn, and Seitz (25) on the diphenylpolyenes, which we have already reproduced in figure 8. Taking the frequencies of the first absorption maxima as given in their table, we have obtained the wave lengths whose squares are plotted in figure 11 against the number of units, n , of the polyenic chain. The very close approach of the individual points to a straight line is an excellent verification of equation 6. The intercept of this line on the n -axis shows that, if we wish to make λ^2 not merely linear with but proportional to n , we must add to the latter the equivalent of 2.35 units for each phenyl group, while Hausser assigned 1.5 units to this group. We attach, however, no importance to this. Our equation was derived for a number of equivalent units. What effect is produced by

ending the chain, or by using different end groups, cannot be predicted. The main thing is that we have linearity of λ^2 with n in the higher values of n . It may be accidental that the points for small n fall on the same line.

Insofar as the statement of Hausser is correct, that some seventy polyenic substances fall on a single curve, such as that of figure 9, we may say that the absorption frequencies may be calculated from a single value of k characteristic of a polyenic chain. Many of the data, however, are far from accurate, and in some of the simpler members of the series Hausser and also Smakula, who published a similar curve, apparently overlooked the faint bands of lowest frequency, such as we shall see in figure 15.

The measurements on the diphenylpolyenes also show an interesting relationship between the number of double bonds and the intensity of absorption. Whether the latter be measured by the maximum extinction coefficient, or by the area under the first absorption band, the authors found the intensity to be a linear function of n . It is tempting to look for general relationships among intensities similar to those found for frequencies, and we realize that in the study of color the intensities and the positions of absorption bands are of coördinate importance. We are obliged, however, in the present paper to neglect in most cases the problem of intensities, to which we hope to revert on another occasion.

The success of the idea of a single oscillator for a whole molecule leads to inquiry as to whether we ever have absorption to the next higher vibrational level than the first, i.e., $\Delta v = 2$. In the ordinary treatment of atomic oscillations, the probability of an absorption of light that carries the oscillator from the level $v = 0$ to level $v = 2$ is found to be zero for a harmonic oscillator, and to increase with increasing anharmonicity. If we carry over this idea to the electronic oscillator, we see that if the energy change from $v = 0$ to $v = 1$ is equal to the energy change in going from $v = 1$ to $v = 2$, or, in other words, if the potential curve is a true parabola, then we cannot expect to find the second-order bands corresponding to the transition from $v = 0$ to $v = 2$. On the other hand, if the potential curve is no longer a parabola, but something like the dotted curve of figure 10, and if the levels come closer together with increasing v , as indicated in that figure, these second-order bands should be observed, and with an intensity depending upon the anharmonicity.

Hausser, Kuhn and Seitz (25) found for the diphenylpolyenes a characteristic band of short wave length which they attributed to the phenyl groups. However, we find quite similar bands in many substances which contain no phenyl group. Thus in figure 12 are shown the absorption curves of various carotinoids given by Smakula (66a), all of which show, and most of which show uniquely, a band in the ultraviolet which would be difficult to account for except by our assumption. We give in table I

Smakula's figures for the first band (band 1), which represents pure first-order electronic absorption, and for band 5 which we are now attributing to second-order absorption. It will be seen that the ratio of λ_1 to λ_5 lies in the narrow range 1.70 to 1.85.

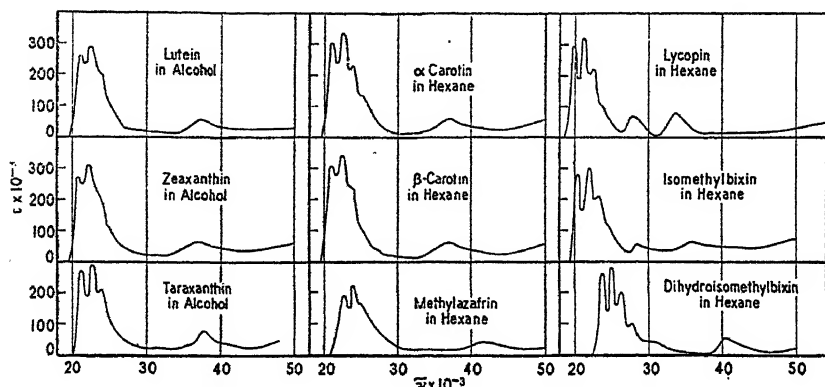


FIG. 12. Absorption curves of various carotinoids

TABLE 1

Values for band 1 and band 5 for some carotinoids

| CAROTINOID | λ_1 | λ_5 | RATIO λ_1/λ_5 |
|--------------------------------|-------------|-------------|--------------------------------|
| Methylazafrin*..... | 442 | 240 | 1.85 |
| Dihydroisomethylbixin..... | 422 | 247 | 1.71 |
| Isomethylbixin..... | 490 | 277 | 1.77 |
| β -Carotin..... | 477 | 270 | 1.77 |
| α -Carotin..... | 475 | 270 | 1.76 |
| Taraxanthin (in alcohol)..... | 471 | 265 | 1.78 |
| Lycopin..... | 504 | 296 | 1.70 |
| Zeaxanthin (in alcohol)..... | 480 | 273 | 1.76 |
| Lutein (in alcohol)..... | 475 | 267 | 1.78 |
| Crocetin..... | 445 | 254 | 1.75 |
| Violaxanthin (in alcohol)..... | 471 | 265 | 1.78 |

* All these substances were measured in hexane solution unless otherwise specified.

Let us now return to the simpler diphenylpolyenes with one, two, three, and four double bonds between the phenyl groups. Here, according to the authors' data, the ratios between corresponding λ 's are respectively 1.39, 1.44, 1.51, and 1.58. Inspection of these figures, together with the average ratio 1.76 for the long-chain carotinoids, indicates that we are really dealing with second-order absorption. For as we go to larger values of n , where the energy levels sink toward the bottom of the potential curve where it is

nearly parabolic, the ratio of the first-order to the second-order wave lengths is approaching 2.

Independent evidence that these are second-order bands of the diphenylpolyenes is furnished by their intensities. It was found that the ratio of intensity of the second-order to the first-order bands diminishes with increasing n . This is to be expected from our hypothesis, for with increasing n we are approaching the purely harmonic region, where the relative intensity of the second-order bands should approach zero. If instead of the parabola we use a curve given by the equation $V = \frac{1}{2} kx^2 + bx^4$ for which the corresponding quantum levels have been evaluated, we find, taking a negative value of b , that the above ratios increase with n , but not so rapidly as the experimental values. It will be interesting to try other functions in which the curve departs even more rapidly from the parabolic form, with increasing displacement.

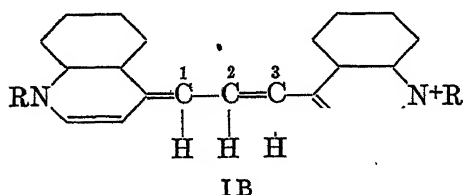
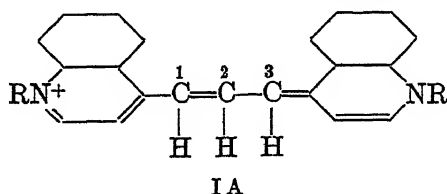
The second-order bands which, like the first-order bands, belong to the fundamental oscillation of the molecule as a whole, and which are to be expected in a great variety of substances, are ordinarily obscured by another type of band, which is due to only a part of the molecule, and which we shall discuss presently under the name of bands of partial oscillation.

Linear oscillators of another type

In discussing the polyenes we have assumed that in the actual resonating molecule, even in the electronically excited states, the electrons never get far from the positions indicated in the classical formula. While we have assumed that the electrons are capable of concerted movements as to phase, we have not supposed the restoring force within a single unit to be appreciably affected by the electrons of the next unit. We might go to the other extreme and assume in certain other kinds of molecules that the electronic cloud is diffuse and more or less uniformly distributed throughout the length of the chain, and that the restoring force is now chiefly dependent upon the position of other neighboring electrons. We should then have an analogy to the longitudinal vibrations in an elastic string, where the frequency is inversely proportional to the length of the string. It is therefore interesting to see whether there are series of nearly linear molecules in which the wave length of maximum absorption is linear with the length of the chain, and whether the constitution of such molecules is such as to suggest a more or less uniform and continuous distribution of the electronic cloud.

In the polyenes we saw that the main contributor to the resonance state was represented by the classical formula (A). Turning now to the carbocyanines and similar dyes, which have been much investigated, the conditions are quite different. For the ion of a cyanine such as is represented

below, we have no one main contributing structure, but two symmetrical structures contributing equally to the resonance state, namely,

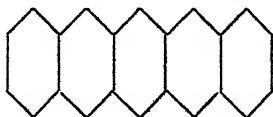


Whatever the electronic distribution may be, it will be the same between atoms 1 and 2 and between atoms 2 and 3. The properties of such a system will be further discussed in the following section.

The best absorption data for substances of this class are those obtained by Fisher and Hamer (19) and Beilenson, Fisher, and Hamer (3) upon a series of carbocyanines which differ only in the number of ethylene groups added to the connecting chain. Again we use the data from the table given by the authors. These data are reproduced in figure 13, where λ is plotted against the number of double bonds lying between the two nitrogens. It is evident that the relation is linear. Similar data have been obtained by these authors and by Brooker and coworkers (7, 8) for other series of similar substances. Apparently within the limits of error the same relationship holds.

Another series of substances in which this linear relationship appears to be valid, although the experimental error is large, was obtained by Hausser (23) by dissolving the diphenylpolyenes in concentrated sulfuric acid. Here the absorption maxima have moved far toward the red. The resonance in this type of molecule will be compared with that in the cyanine type, in the following section.

Finally we may mention an entirely different class of substances, the linear condensed ring systems (13), from benzene to pentacene,



Here we are dealing again with neutral molecules, but with a high degree of conjugation. As far as we can gather from the existing experimental data,

λ seems to be roughly linear with the number of rings, indicating that here also the electronic cloud is diffuse and not much localized.

Between the two types of linear molecules represented by the polyenes and the cyanines we may expect to find many intermediate substances, especially such compounds as have, in the part of the molecule in which oscillation occurs, a charge which is less than unit charge. Sufficiently exact data for testing this supposition are at present lacking. Still another type of nearly linear molecules, the *p*-polyphenyls, will be discussed in the next section.

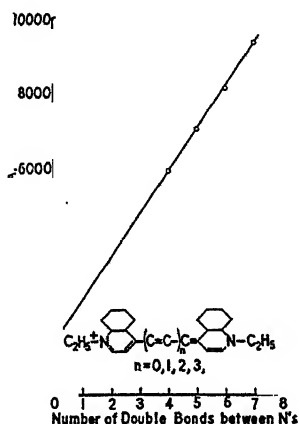


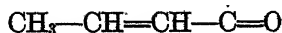
FIG. 13. Plot of wave length against the number of double bonds between the two nitrogen atoms for a series of carbocyanines

FURTHER REMARKS ON CONJUGATION

The important effect of conjugation on absorption has already been illustrated in figures 6 and 7. The latter figure shows that, when a molecule has two double bonds which are insulated from each other, each will show its own absorption; so also in figure 14 (57) we see the effect of such insulation between two carbonyl groups. Curve 2, for dipropionylethane, is almost identical with the dotted curve 3, which shows twice the absorption coefficient of acetone. On the other hand, curve 1, for the conjugated diacetyl, shows a powerful fundamental absorption at lower frequencies, as well as a "partial" band not far from the other curves.

These fundamental bands of the whole conjugated system, which are so pronounced in dyes, may in simpler molecules be of such low intensity as to be frequently overlooked. Thus in the case of crotonaldehyde (figure 15),

H



which has been studied by Lüthy (45), the weak fundamental band, which is less than one-thousandth as intense as the next band at higher frequency and would not be seen except on a logarithmic plot, was missed completely by Smakula in the tabulation to which we have referred.

Similar conditions are found in the case of benzene, whose absorption spectrum has been more thoroughly studied than that of any other substance, chiefly in the range between 2300 and 2800 Å. The absorption in

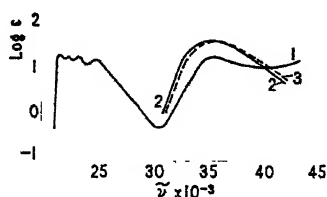


FIG. 14. Effect of insulation of carbonyl groups on the absorption. Curve 1, $\text{CH}_3\text{COCOCH}_3$ in hexane; curve 2, $\text{C}_2\text{H}_5\text{COCH}_2\text{CH}_2\text{COC}_2\text{H}_5$ in hexane; curve 3, CH_3COCH_3 in hexane ($2 \times \epsilon$).

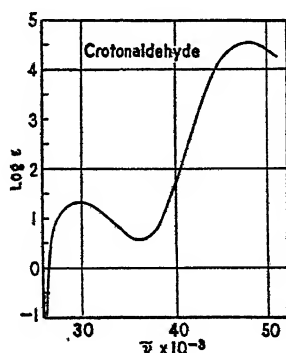


FIG. 15. Absorption curve of crotonaldehyde.

this region, however, is very small compared with that at higher frequencies. The bands of ethylbenzene (which are almost identical with those of benzene) and of styrene are shown in the two diagrams given by Smakula (66b), which we reproduce in figure 16. In the dotted curve the extinction coefficients have been multiplied fivefold, in order to show how weak is the fundamental absorption band of ethylbenzene compared with that of styrene, the latter being one of the first members of the highly conjugated series that we have already discussed.

The weak absorption of benzene, in its conjugation band, shows that the phenomena of color and of resonance, although they are closely related, are not related in such a way that high resonance energy implies large absorption of light. The chief resonance of benzene is the sort in which there are two major contributing structures of equal importance, the two Kekulé structures; but this resonance does not directly contribute to light absorption. It is only the minor contributing structures, such as may be represented by the formulas



that are involved in the absorption. Insofar as these ionic structures become important, they diminish the Kekulé resonance and, conversely, the great strength of the Kekulé resonance diminishes the contribution of the ionic forms.

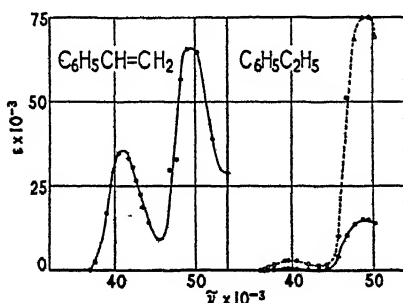
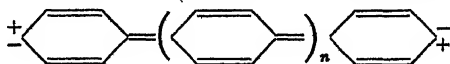


Fig. 16. Absorption curves of styrene (left) and ethylbenzene (right)

The same principle applies to the polyphenyls. The only two structures which are concerned with light absorption are expressed by the formulas



but these formulas require a completely quinoid condition and therefore can exist only at the expense of the numerous types of Kekulé resonance.

When the number of phenyl groups in the chain is small, the large percentage increase in length produced by one additional phenyl group, will produce so large a change in the polarizability as to offset the counter-acting tendency of the Kekulé resonance and we should expect a considerable increase in the wave length of the absorption maximum. On the other hand, when the chain is already long, each new phenyl group will produce only a relatively small increase in length; but the electronic oscillation, if it is to run through the whole molecule, must do so at the expense of two new Kekulé resonances for each group added.

Gillam and Hey (20a), in a very recent article, have determined the wave length of maximum absorption of five *p*-polyphenyls in chloroform. Their results are as follows: diphenyl 2515 Å; terphenyl 2800 Å; quaterphenyl 3000 Å; quinquiphenyl 3100 Å; sexiphenyl 3175 Å. Presumably further increase in the length of the chain will produce little change in the *position* of the absorption band. The essential difference between the conjugation in the polyphenyls and in the polyenes may be brought out by considering the effect of inducing a positive charge on one end of the chains. What we may call the center of gravity of the residual negative charge will, in the polyenes, move away indefinitely as the length of the chain increases. In the polyphenyls it will move out through a few groups only, and then be nearly stationary as the chain is indefinitely increased.

Bands of partial oscillation

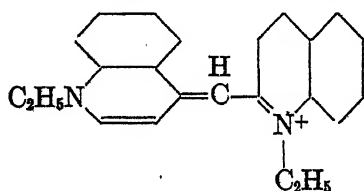
In such figures as we have presented, showing the fundamental band due to the whole conjugated system, and another band of higher frequency, we can conceive the latter to be due to a localized oscillation in some part of the molecule, involving in some cases only a single chromophore. These bands of partial oscillation are not our primary concern, but since we shall mention them occasionally they may briefly be discussed here. When there is insulation between two chromophoric groups,—for example, when they are separated by one or more saturated carbon atoms as in figures 7 and 14,—their oscillations are independent. However, when we have two conjugated double bonds, even if we are able to stimulate an oscillation in one of them alone, we need not expect to obtain the absorption which that double bond shows when isolated, for the process of conjugation or resonance has changed the energy of the whole molecule. Nevertheless by its form and position we are usually able to identify approximately these bands of partial oscillation with the bands of the individual chromophores, as we see in figure 15.

The question now arises as to the relative intensity of the bands of total and of partial oscillation. In the process of conjugation a certain amount of energy is set free which is known as the resonance energy. If we divide Planck's constant h by this resonance energy, we have a number which has the dimensions of time, and it is occasionally useful to consider that this number gives the order of magnitude of the time required to establish in the molecule the normal conditions of the resonance state.

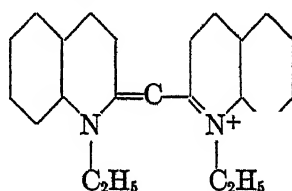
The resonance energy of a conjugated diene amounts to several kilocalories, which gives for the resonance time a value between 10^{-13} and 10^{-14} sec. Now the period of the light which is absorbed by butadiene is of the order of 10^{-15} sec. The fact that the period of light is short compared with the period of resonance may explain the observation that, as we

proceed farther into the ultraviolet, all absorption spectra appear to an increasing degree to be characteristic of individual chromophores. On the other hand, in the case of dyes which absorb in the visible, where the period of the light is greater and the time of resonance, because of large resonance energies, is shorter, the absorptions are characteristic of well-conjugated systems acting as single units.

These bands of partial vibration are almost invariably to be found in the ultraviolet, where they are usually to be ascribed to simple chromophoric groups, such as the phenyl or vinyl groups, but they are also to be found in the visible, where they belong to large parts of an extensive conjugation. We shall illustrate this by means of the absorption curves obtained by Brooker and Smith (8) for a number of cyanines. In the accompanying set of formulas, I and II represent isocyanine and pseudoisocyanine, while III is a more complex structure containing, in a sense, both I and II.

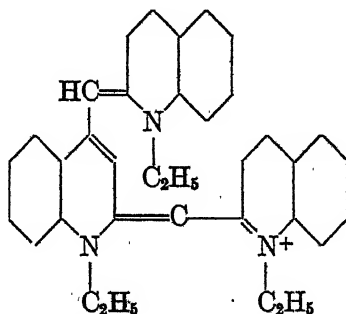


Isocyanine ion



II

Pseudoisocyanine ion



III

2,4-Di[(1-ethyl-2(1)-quinolyldene)methyl] (1)ethyl quinolinium ion

In each case only one of the resonance forms is given. The main contributors to resonance may be obtained by assigning the positive charge to any one of the nitrogen atoms. The absorption curves are shown in figure 17. The two isocyanines give the entirely similar curves 1 and 2. We shall reserve our comments upon the double peaks until we discuss later an important paper by Scheibe. In curve 3 we see the important new band in the red, which we ascribe to the electronic vibration in the molecule

as a whole. It seems very reasonable to ascribe the right-hand portion of this curve to a partial oscillation, belonging to that part of the molecule which is similar to structure I, or to that part which is similar to structure II, or to a merging of the two. The fact that this part of the curve appears at higher frequency than in curves 1 and 2 is an illustration of a very general principle, which will be treated later under the head of cross conjugation.

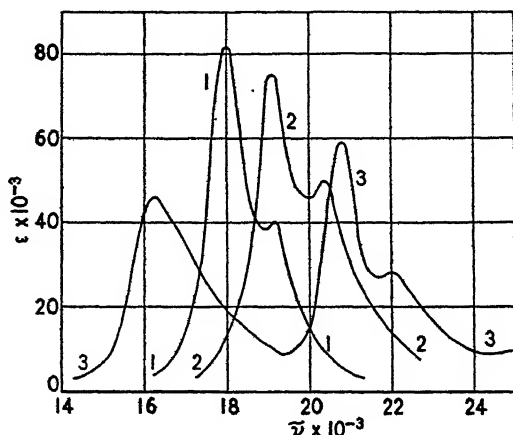
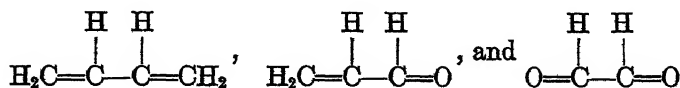


FIG. 17. Absorption curves of a number of cyanines. Curve 1, isocyanine ion in ethanol; curve 2, pseudoisocyanine ion in ethanol; curve 3, 2,4-di[(1-ethyl-2(1)quinolyldine)methyl]-1-ethyl quinolinium ion in ethanol.

Relations between the absorption of a conjugated system and of its component parts

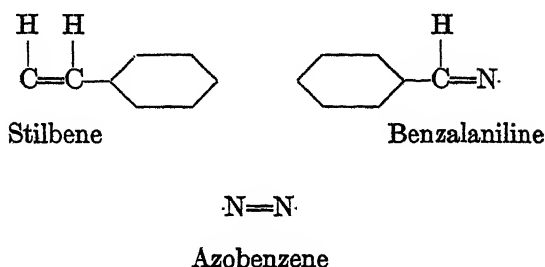
We have not succeeded in finding any way of calculating quantitatively the absorption frequencies of conjugated molecules from those found for the individual component double bonds, nor are there any data sufficiently accurate to test such a calculation. Qualitatively, however, we may predict, from our idea of strain, the absorption of numerous types of conjugation.

The frequency of absorption will be lower when the electronic displacements are such as to diminish the double-bond character in bonds of high strain, and higher when the displacements increase the double-bond character in such bonds. Thus the double bonds $C=C$, $C=N$, $C=O$, $N=N$, and $C=S$ will lower the absorption frequency in this order. In the three molecules



the absorption maxima are approximately at 2200, 3500, and 4600 Å.

The three substances, stilbene, benzalaniline, and azobenzene have



progressively lower absorption frequencies. The first absorption maxima are, respectively, about 3100, 3300, and 4500 Å.

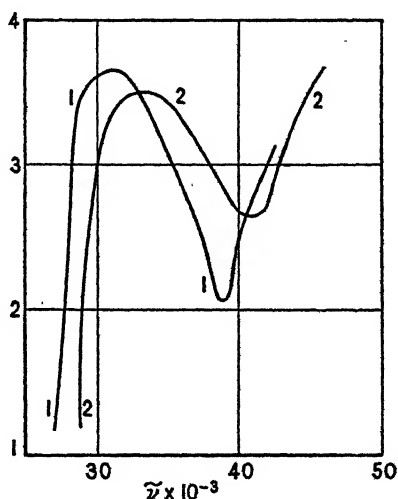
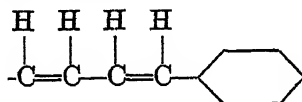


FIG. 18. Absorption curves of diphenylbutadiene (curve 1) and benzalazine (curve 2)

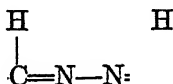
The strongest of these chromophoric groups, or, in other words, the one that we consider to be in the state of greatest strain, is $\text{C}=\text{S}$. It gives colored compounds even of such simple type as thioacetophenone and thiobenzophenone. The latter has an absorption maximum at 6200 Å. (9).

An interesting corollary follows from our statement that $\text{N}=\text{N}$ is more chromophoric than $\text{C}=\text{C}$, because of the strain which favors the ionic contributors to resonance. We should find, in a conjugated system which in its ordinary form is written with a single bond between two nitrogen atoms, that the absorption frequency is higher than in the corresponding compound with carbon atoms, for in this case the ionic forms can only occur when the highly strained double bond is produced between the two nitrogen atoms. This is true, as shown, for example, by figure 18, which

reproduces the results of Rădulescu (55) on the two compounds



and



The first, purely ethylenic, substance gives curve 1, whereas the second substance, with the N—N bond, absorbs at higher frequency (curve 2).

Steric effects on conjugation

The degree of conjugation, and therefore the mobility of electrons, in a system may depend not only upon the nature of the double bonds but also upon certain steric relations.

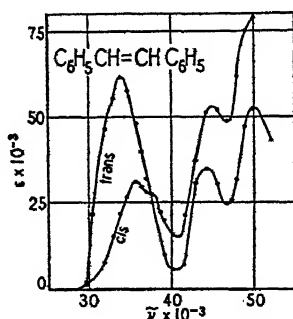


FIG. 19. Absorption curves of the *cis*- and *trans*-forms of stilbene

If we construct in space a model of the molecules of *trans*- and *cis*-stilbene we see in the latter case that, if we use the proper bond distances and angles, two of the ortho hydrogens of the benzene rings are presumably brought sufficiently close to exert upon one another a considerable repulsive force. This will tend to force the system out of a plane, with the effect of reducing resonance.

The optical effects are shown in figure 19 (67), which shows the absorption curves of these two substances. The effect of the powerful conjugation of *trans*-stilbene is shown both in the position and in the intensity of its fundamental band.

Even in *trans*-stilbene, when the hydrogen atoms are replaced by one or two methyl groups, these methyl hydrogens come close enough to the benzene ring to produce a similar effect, as shown in figure 20 (43), in which

the first curve is that of stilbene, and the second and third are those of the mono- and dimethylstilbenes.

Finally, when we come to some of the ortho-substituted biphenyls, the bands of conjugation disappear when there are four methyls or four chlo-

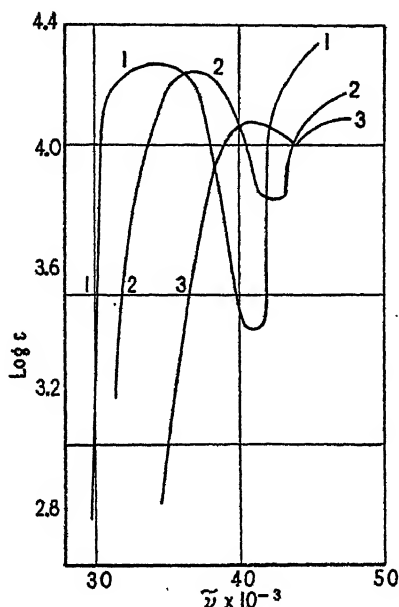
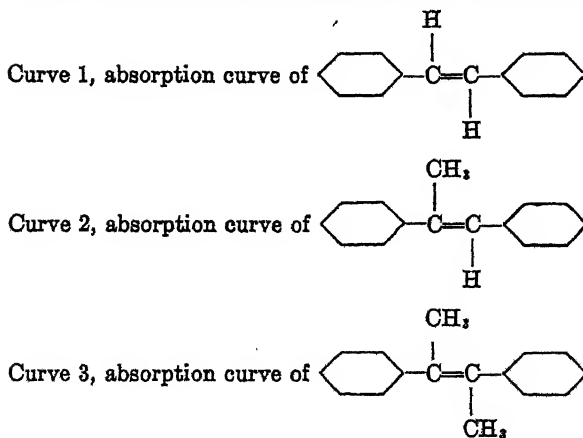


FIG. 20. Absorption curves of stilbene and methyl stilbenes



rines in the ortho-positions, as shown by Pickett, Walter, and France (52). Here no approach to the planar structure is possible, and the authors themselves remark, following a suggestion of Kistiakowsky, that the

differences in the spectra "may be dependent on the planar form of the molecule."

Evidence of the diminution in resonance by steric influences which prevent coplanarity has been drawn from chemical behavior by Calvin (11) and from dipole moments by Birtles and Hampson (5) and by Ingham and Hampson (34).

GENERAL RULES OF COLOR

Since the original chromophore and auxochrome theory of Witt, there have been very few theories of color that have proved applicable to more than a limited group of dyes. A theory of Dilthey (18), which has been strongly emphasized by Wizinger (71), deserves our attention. According to this theory, while other types of substances show weak absorption, running well into the visible region, by far the most powerful absorbers of visible light are "ionoid." There is no doubt that this is a very important observation, but it can at best be only a partial statement of a more general principle, even with the most liberal interpretation of the word "ionoid." Wizinger implies that the strongly colored substance must be an ion or an inner salt, but this must be incorrect, as may be seen immediately when we consider the so-called, halochromic phenomenon. A vast number of neutral organic substances become brilliantly colored upon the addition of hydrogen ion (51), but these same substances absorb with approximately the same intensity and at almost the same frequency when neutral substances such as boron trichloride or stannic chloride are added in place of hydrogen ion; yet in these cases the resulting molecules are not ions. Also, it should be pointed out that neutral substances such as *p*-nitroaniline or 4-nitro-4'-aminostilbene, both of which are yellow to orange-red, lose their color or become only a pale yellow upon the addition of hydrogen ion.

Let us see whether it is possible to establish the general principles underlying the phenomenon of color, from our theory of electronic oscillations. We may visualize a sort of "ideal" molecule in which every electron-pair is situated in so deep a potential trough that it can be excited to a higher energy state only by the addition of a large amount of energy. The nearest approach to such an ideal molecule is furnished by the aliphatic hydrocarbons. Even in these cases we have seen that there is a diminution in the energy required for excitation when a ring is formed (see figure 6), and this effect doubtless increases in accordance with the Baeyer strain theory until we reach the three-membered system of cyclopropane, and indeed until we reach the two-membered system of ethylene. We may conceive that, even in these simple cases, that which we call a state of strain has moved some of the electron pairs into positions where excitation is more easily effected.

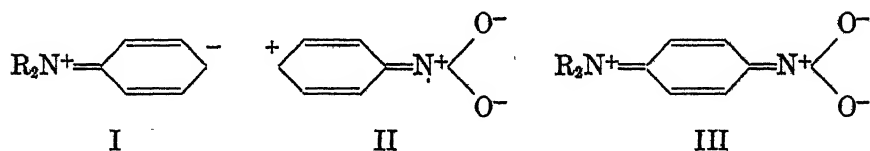
The fact that cyclopentadiene absorbs at a lower frequency than butadiene, as illustrated in figure 6, may be attributed to the increased strain and therefore the increased energy of the classical structure. So we have found it convenient to assume an increasing strain in the series of double bonds from $C=C$ to $C=S$. The effect of these strains is to move the normal state of the molecule away from the more ideal condition represented by the classical formula.

We are assuming that *every displacement from the ideal state makes further displacement easier*, or, in other words, increases the mobility of electrons. We have already given one example of this in studying the polyenes, where we were led to the conclusion that increasing the displacement caused a diminution in the coefficient of restoring force.

One way of viewing this phenomenon is to think that the electronic clouds are highly localized at the places where electron-pairs appear in the classical structure, but that they become diffuse, and more uniformly distributed, when there is any displacement from that structure. We then associate this increased diffusion with a higher mobility and with a lower value of the restoring force constant.

Thus if we wish to produce a bathochromic effect in a molecule (a) we may increase the masses of the oscillating system by increasing the number of participating electrons, which may be accomplished by increasing the extent of the conjugating system, as in the polyenes or the phthalocyanines, or (b) we may increase the mobility of the electrons. We may now see how this mobility may be increased in the several important classes of substances.

The first case we must deal with is the one in which we start with a resonating molecule, in which the main contributor is a classical structure such that no atom has a formal electric charge. Here one of the most important methods of producing a bathochromic effect is by the use of an auxochrome. Benzene is such a molecule. If we substitute for one of the benzene hydrogens a basic auxochrome, such as NR_2 , or an acid auxochrome, such as NO_2 , we have new resonating states in which there is a shift toward the resonating forms I and II.



If the benzene ring has both these auxochromes para to each other as in formula III, we have a much greater contribution from the polarized form, and the electronic center has been moved much farther to the right. The

fact that the dipole moment of *p*-nitroaniline is considerably greater than the sum of the moments of nitrobenzene and aniline may be regarded as an illustration of the principle that a displacement from the "ideal" molecule renders further displacement easier. Even in *p*-nitroaniline the equilibrium center of the electrons is still far removed from that which would be found if the molecule actually had structure III, as shown by the fact that the dipole moment is only about one-fifth of that which would be calculated for the complete inner salt. All of these substitutions increase the mobility, especially in *p*-nitroaniline whose absorption band reaches into the visible region.

There has been a widespread belief that the dielectric constant of the medium has a large influence upon absorption curves. We do not see that

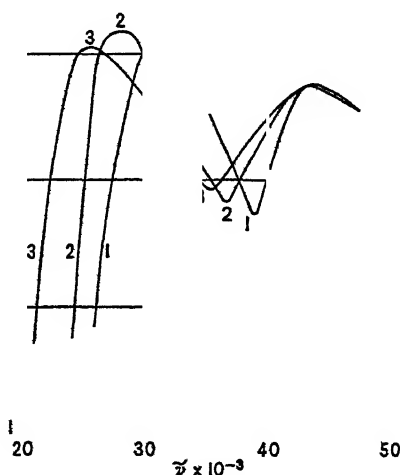
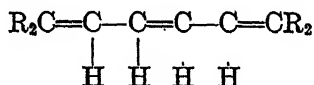


FIG. 21. Absorption curves of *p*-nitroaniline in hexane (curve 1), dioxane (curve 2), and water (curve 3)

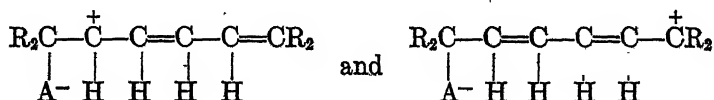
this should be so, nor in general do the experiments seem to indicate that it is so. However, in such cases as the three that we have just considered, we not only expect and find such an influence, but these examples provide an excellent further illustration of our principle that electron mobility increases with increasing departure from the ideal state of the classical structure. In these substituted benzenes the contribution of the ionic forms becomes greater if the energy required for the separation of charges becomes less, as happens in a solvent of high dielectric constant. This further displacement from the ideal molecule has the effect of increasing the mobility according to our principle. This is illustrated in the absorption curves of *p*-nitroaniline in (1) hexane, (2) dioxane, and (3) water, as shown in figure 21 (16). It is to be emphasized, however, that the ionic

forms in such substances as the polyenes are not much favored by a solvent of high dipole moment; since the resonance state has no average moment, and the motions of the electrons are too rapid to be followed by the dipoles of the solvent.

Starting again with a molecule in which the chief resonance contributor is a classical structure, we can produce a greater bathochromic effect than is caused by any ordinary auxochrome, by adding an acid, or in rare cases a base, to one end of a double bond that is part of a conjugating structure. The effects upon absorption are the same qualitatively and usually quantitatively, whether the added acid is hydrogen ion or one of the generalized acids (37) such as boron trichloride or stannic chloride. We have seen in the preceding section the enormous bathochromic effect when the polyenes are dissolved in concentrated sulfuric acid. Identical colors are obtained by treating them with boron trichloride (39). Let us examine what happens to the resonance within the molecule in this case, which is one of the simplest examples of the important halochromic phenomenon. Take the polyene



In the resonating molecule by far the most important contributing structure is the one written. Supposing now that the neutral acid A is added at the first carbon atom; then we have a series of resonance structures such as

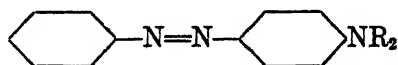


in which the positive charge is placed on the second, fourth, or sixth carbon atom. Perhaps the last structure contributes most, but they are all important, and no one of them even approximates to an ideal molecule. The result is that a molecule in which electron-pairs were capable of only small motions about definite positions has now been converted into a molecule in which the electron cloud has become diffuse and which approaches, but does not reach, the state about to be described.

We now come to the class of substances which includes the great majority of powerful dyes, and which presumably Dilthey had chiefly in mind when he proposed the "ionoid" theory. It is the class we have already had exemplified by the cyanines, in all of which the intense color is due to an ion in which the charge may equally well be placed at either end of a chain, and practically all the resonance may be regarded as between the two opposite forms. If we were able to plot the density of electronic cloud in

the molecule, it would presumably be very diffuse and certainly would show no distinction between those places where we arbitrarily place double or single bonds. The condition is not very different from that in the polyenes dissolved in sulfuric acid, except that there the density of electrons more or less uniformly diminishes from one end of the molecule to the other, whereas here we have a uniform condition along the chain, especially if the two end groups are identical. Even if the end groups are not the same but yet are of the same general character, the same conditions prevail. This is shown by the fact that Beilenson, Fisher and Hamer (3) were able to calculate with moderate accuracy the absorption of hybrid cyanines with a group A at one end and B at the other, from the spectrum of the A, A and the B, B dyes.

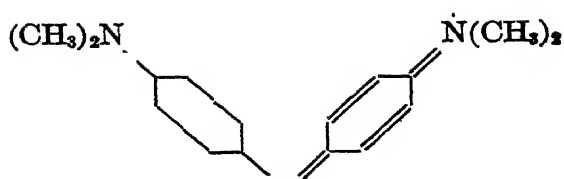
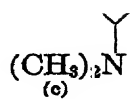
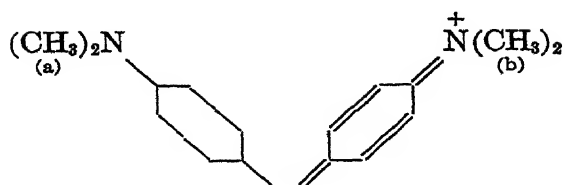
Most of our common acid-base indicators are substances which, when they are in their more strongly colored form, have acquired a charge which is not confined to one place in the molecule but rather appears, in different phases of resonance, in distant parts of the molecule. Thus the indicators of the type



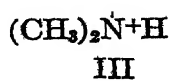
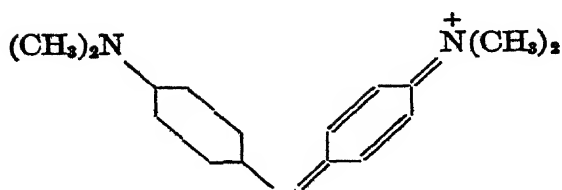
are well-conjugated molecules, as shown by their yellow color in the neutral state. This resonance, however, is one in which a single classical structure is the main contributor. When hydrogen ion is added to the nitrogen atom farthest to the left, an intense red color appears. The chief resonance is now between two structures, one of which has the positive charge on that nitrogen, while the other has it on the amino nitrogen.

Schwarzenbach (63) has made a careful study of a number of indicators which exhibit several successive color changes, and has shown that the highly colored forms are always the ones in which the charge may equally well be placed at one extremity or the other of a symmetrical molecule. He has also pointed out that these highly colored forms are also the more stable, but this is not always the case. This point has been brought out in our discussion of benzene, and will now be further illustrated, as we offer an explanation of what has seemed a striking anomaly in the theory of color (71).

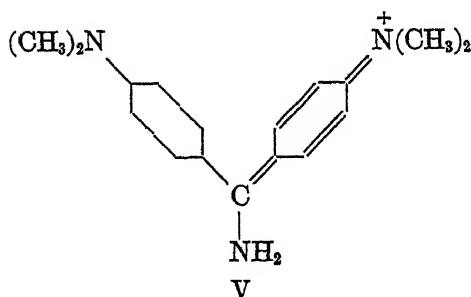
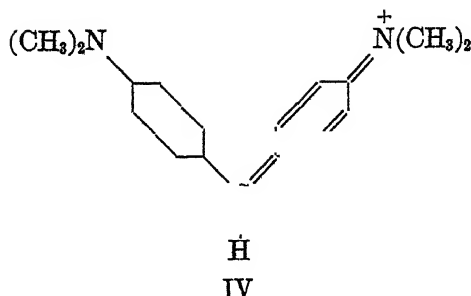
The ion of crystal violet (I), p. 309, is a highly resonating molecule. The three chief contributing forms, all alike, are obtained by assigning the positive charge in turn to the three nitrogen atoms. As evidenced by its chemical behavior, it has far more resonance energy than malachite green (II), but while the absorption band of crystal violet has a maximum at 5900 Å., that of malachite green lies at 6230 Å. This is not an isolated phenomenon, but many cases could be cited; for example, as acid is gradually added



II



III



to crystal violet, its chief absorption moves first toward the red and then toward the violet, as we have seen in figure 2. In substance III, produced by adding one hydrogen ion to the ion of crystal violet, the absorption maximum lies at 6300 Å. Also we have studied (73) the absorption of the ion of Michler's hydrol (IV). Its absorption maximum is at 6200 Å. In these three substances—II, III, and IV—the resonance energy of crystal violet has been reduced by varying amounts, but they show nearly identical absorptions, all at higher wave length than that of crystal violet (I). We may also compare compounds IV and V (auramine). In the latter, although hydrogen has been replaced by the amino group and thus the possibilities of resonance have been increased, the absorption is nevertheless at a far lower wave length, namely, 4200 Å. (36).

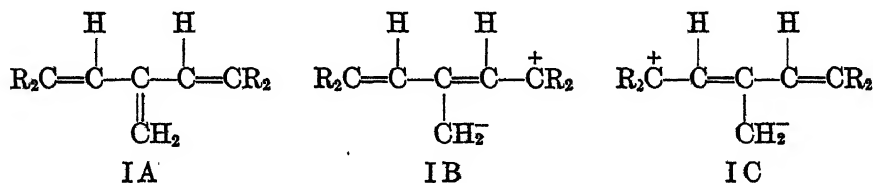
The explanation of these facts from our present point of view is an extremely simple one. If we add the auxochrome NR_2 to malachite green or to Michler's hydrol, to form crystal violet or auramine, we have increased the resonance by increasing the number of important resonance forms. The positive charge in the former pair can be considered as belonging to either one nitrogen or the other. In the latter pair it may be shared by all three nitrogens. While this increases the resonance, it does not favor the resonance that is responsible for color.

Consider in formulas I to V a horizontal axis which represents the direction of an electronic oscillation. In form I we have a positive charge which

belongs collectively to the three auxochromes. Those phases, however, in which this charge is on auxochrome *c* do not contribute to the horizontal oscillations between auxochromes *a* and *b*. We may say roughly that only two-thirds of a charge is capable of this *ab* oscillation. In formulas II, III, and IV, on the other hand, we have a full charge capable of oscillating horizontally. When we come to formula V, it is presumable that the nitrogen on the central carbon atom can be assigned more than one-third of the positive charge. All of these statements are in complete accord with the observed colors. We have referred to a similar case in discussing figure 17. Regarding electronic oscillations in the vertical direction we shall have something to say in a later section.

The ideas just illustrated may be formulated in a general principle. When the color of a substance is associated with an oscillation along a certain path in the molecule, and when it is due to an excess charge (positive or negative) which may move toward one or the other ends of this path, then the frequency of absorption will be increased by any influence that diminishes the amount of that charge, and decreased by any influence that makes this charge larger.

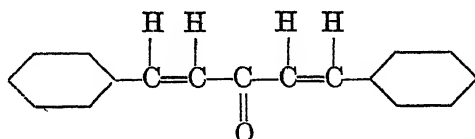
We may apply this principle to explain the remarkable effect of cross conjugation upon color. Let us examine the substance represented by formula IA.



At first sight it would appear that the oscillations should be extremely limited, namely, through the central double bond to the right or through the central double bond to the left, yet this substance absorbs at much lower frequency than a straight-chain triene. We must, however, remember that two of the contributing structures are those in which the central double bond is broken, leaving the lower carbon atom negative or positive, and therefore forcing an excess positive or negative charge into the rest of the molecule. To illustrate the first case we write the formulas IB and IC which, because of their symmetry, contribute equally to resonance, and also because of their symmetry increase the tendency to break the central double bond. Now since the forms IB and IC are analogous to the structures of the cyanine ions, we see that, insofar as they contribute to the actual resonance state, they will have a strong bathochromic effect.

Similarly we might consider substances of the type of phorone, in which the central double bond goes to oxygen instead of to CH_2 . In such com-

pounds the oxygen, because of its strong tendency to become negative, contributes a considerable positive charge to the main axis of oscillation. The absorption bands extend into the visible. An interesting group of similar substances is found in dibenzalacetone and its derivatives.



Dibenzalacetone

These substances are colored, usually yellow, and it is evident that the transfer of excess positive charge into the horizontal, well-conjugated chain represents a very important contribution to the actual state of resonance. We can form an idea of the amount of this contribution when we forcibly destroy the central double bond by the addition of an acid to the oxygen. We get the same colors (39) whether this acid is hydrogen ion or boron trichloride. However the change of color is not great; we estimate roughly that the absorption maximum is carried about 1000 Å. toward the red when acid is added to dibenzalacetone, dipiperonalacetone, and dianisalacetone. In other words, even before the addition of acid the resonance form in which the carbonyl double bond is broken is a major contributor to the resonance state.

This strong tendency to break the double bond, which we here observe in the case of $C=O$, we should expect, from our earlier considerations, to be even more marked with $C=S$. This has been found by Burawoy (9), who obtained the absorption spectra of the compounds $((CH_3)_2NC_6H_4)_2C=X$, where X is CH_3 , NH , O , or S . The bathochromic effect increases in this order, and is very large in the case of sulfur.

The most important dyes, except those ions in which the charge may oscillate from one part of the molecule to another, belong to the anthraquinone and indigo types. These all contain carbonyl groups, and it seems reasonable to suppose that the general marked chromophoric character of the carbonyl groups is closely analogous to the effect that we have been discussing.

Summary

Let us summarize the theory of color that we have been developing. Light absorption is due to the excitation of electronic oscillations. In a molecule of the "ideal" type such as a paraffin the energy of excitation is high, but diminishes as the molecule is strained. A great strain is produced by double bonds, which differ from each other in this regard.

Color ordinarily appears in conjugated systems, where the two deter-

mining factors are (a) numbers of electrons involved, and (b) electron mobility. The mobility is small in a molecule whose properties correspond to a formula in which all electrons are paired and there is no "formal" charge on any atom. When such a structure is the major contributing form of a resonating molecule the mobility is still small. When, however, the actual state of a molecule differs considerably from a classical or ideal structure the mobility is greatly increased. In other words, displacement from the ideal structure makes further displacement easier. Strong color is obtained when two important resonance forms are such that the change from one to the other involves the movement of an electric charge. This is a unit charge in many dyes of the ionic type; but there are many neutral dyes in which that part of the molecule in which an oscillation can occur acquires some positive or negative charge from the rest of the molecule. In such cases any change in the molecule which increases that charge enhances the color of the molecule.

ORIENTATION OF ELECTRONIC OSCILLATIONS WITHIN THE MOLECULE

It has long been known that an intimate relation exists between the orientation of a molecule and that direction of polarized light which shows the maximum absorption. This relation has been studied most unambiguously in crystals for which x-ray data show the relative positions of the atoms. We may quote from Hartshorne and Stuart (22): "The study of colored crystals by x-ray methods has revealed how this pleochroism is related to their structure. In organic crystals, the absorption is greatest when light is vibrating along the direction of the bonds in the chromophore groups. . . . Thus in *p*-azoxyanisole, when the vibrations are parallel to the length of the molecule, i.e., to the N=N double bond, the light is yellow, and when the vibrations are transverse, it is colorless." Such work as that of Bernal and Crowfoot (4) on *p*-azoxyanisole, upon which this statement was based, is of an arduous type, and few examples of a complete analysis are available. For this reason more rapid, although less definite, observations have frequently been made by orienting dyes in or on an anisotropic film, such as cellophane (35).

In our previous discussion of long molecules we did not specify the precise direction of the electronic oscillation. In the longer cyanines there is no distinction in the actual molecule between single and double bonds, since the two main resonating structures are entirely similar. There can hardly be any question therefore that the direction of oscillation coincides with the molecular axis. This is by no means so evident in the case of the polyenes, for there the major contributing structure consists of definitely alternating double bonds in a zigzag, in which all the double bonds are parallel. Now since we have assumed that, even in the excited state,

the displacements of the electrons are not large, it might be concluded that the axis of oscillation would lie between the axis of the molecule and the line which is parallel to the double bonds in the classical structure. Using the x-ray data of Hengstenberg and R. Kuhn (30), Calvin (73) has made preliminary observations on diphenyloctatetraene and diphenyldodecahexaene, which show that the maximum absorption is observed when the electric vector of polarized light is approximately along the axis of the molecule. On the other hand, we are informed by Professor Bernal that W. H. Taylor has examined the entirely similar substance β -carotin, and finds that the vector of maximum absorption is in a direction more nearly corresponding to the line parallel to the double bonds in the classical formula.

When we come to molecules that have considerable extension in more than one direction, our theory of electronic oscillations leads to very definite conclusions regarding the relative orientations of the molecule and of the vector of the exciting light. We have distinguished between the

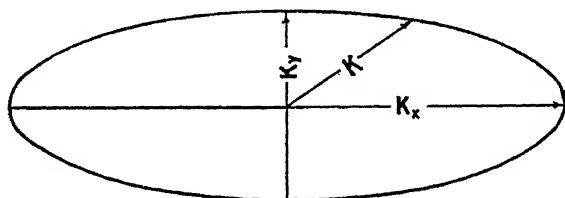


FIG. 22

fundamental bands of the molecule as a whole and the bands of partial oscillation, which concern only a part of the molecule or an individual chromophore. Regarding the latter type of bands we have little information as to the direction of oscillations. A large and important field of investigation with polarized ultraviolet light is almost entirely unexplored. We may predict that when a substance has a series of bands, of which one is a fundamental and the others represent partial oscillations, which may be roughly ascribed to individual groups, the directions of polarization for maximum absorption of two partials will be determined only by the relative orientation of the two groups.

With the fundamental bands the conditions are quite different. Here we have assumed that the oscillations within the molecule may be regarded as the equivalent of a single oscillator in quasi-harmonic motion. In such a case, if we have a planar molecule, the restoring force constant may be different in different directions, as shown in figure 22. Plotting it as a vector, it determines an ellipse, so that by choosing suitable coördinate axes, k is at a maximum in the x direction and at a minimum in the per-

pendicular y direction. The oscillations resolve themselves into independent oscillations of frequency ν_x and ν_y such that $\nu_x/\nu_y^2 = k_x/k_y$. (The figure has inadvertently been drawn so as to make k greater in the x direction, but our normal procedure will be to call the band of lowest frequency the x band.)

We may therefore expect to find for a planar molecule, with no center of symmetry, two fundamental electronic bands at different frequencies, one of which will disappear when the electric vector of polarized light is in the y direction, the other when it is in the x direction.

Some observations with crystals may be pertinent. Taylor (68) has found with crystals of methylene blue a maximum blue color with one direction of polarized light and a maximum brown color in a perpendicular direction. Calvin (73) has likewise found, with crystals of cyanine, green and red colors with maxima in directions also at 90° to one another. The interpretation of these facts is, however, not quite certain and may involve the z bands, which we shall mention presently.

When we have spoken of the independence of the x and y oscillations we have not meant to imply that the y oscillations of higher energy may not go over into the x oscillations by a process of dissipation, in which atomic vibrations which are along neither of these axes participate. Such dissipation will be the subject of the next section. It is a common observation that, if any fluorescent substance is excited by light of far higher frequency than its fundamental absorption band, it emits the same light as if activated in this band itself.

A remarkable phenomenon has been found when fluorescence is produced by polarized light. Ordinarily under these circumstances it has been found, as we should expect, that the reemitted light is polarized to some extent in the same direction as the exciting light. However, Wawilow (69) found that in the four substances rhodamin B, magdala red, aesculin, and fluorescein, the degree of polarization of the fluorescent light diminished with increasing frequency of the exciting light and actually became negative in a certain region, increasing again to positive values at still higher frequencies. In the case of fluorescein the greatest negative polarization occurred at about $32,000\text{ cm}^{-1}$. Now the absorption spectrum of fluorescein in alkaline solution, according to Wrzesińska (72), is given in figure 23. It will be noted that there is an important band with a maximum at about $31,000\text{ cm}^{-1}$ and we have no doubt that this is the y band corresponding to the same fundamental oscillator as the x band at about $20,000\text{ cm}^{-1}$. Let us consider a molecule of fluorescein oriented as in figure 23, that is, with the x direction in the line through the three rings. A beam of light normal to the plane of the molecule and polarized in the y direction can excite only the y oscillation. If, before the molecule has had

opportunity to turn, the energy of the y oscillation is partly dissipated and partly converted into an x oscillation, and the energy of this oscillation is now emitted as light, the polarization observed in the line of sight will be mainly in the x direction, which is the phenomenon observed. Similarly if the light beam is in the x direction and the polarization of the absorbed light in the y direction, the emitted light will be polarized in the z direction, i.e., once more normal to y .

Whenever a planar molecule has no center of symmetry, and it appears from the formula that the value of k should not differ very greatly in the two normal directions, we may expect to find these x and y bands. Let us compare the absorption spectrum of the symmetrical crystal violet with that of malachite green, which has an amino group on only two of the benzene rings. Without discussing at the moment the possible resolution of the bands, crystal violet has only one broad band in the visible.

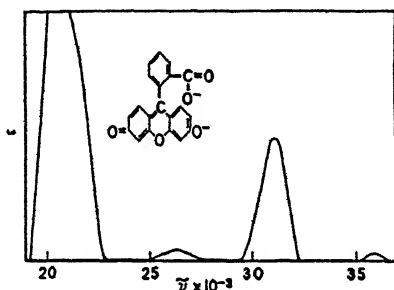


FIG. 23. Absorption spectrum of fluorescein

Malachite green has a broad band with a maximum at $\lambda = 6230 \text{ \AA.}$ and a weaker band at $\lambda = 4300 \text{ \AA.}$ An attempt to find the orientation of these bands by the method of fluorescence polarization is in progress.

When we come to molecules which have a high degree of polarizability in three directions, that is, ones for which the ellipse representing k is replaced by an ellipsoid, we have only two examples to offer, both given by Scheibe (59, 62) in a paper which has interested us greatly, not only because of the importance of the experimental results, but also because Scheibe's interpretation largely coincides with the ideas that we are here developing.

Scheibe studied crystals of naphthacene (2,3-benzanthracene) and found the familiar bands 4750, 4450, 4200 \AA. , which represent the structure of the fundamental electronic band. Absorption in this region is at a maximum when the beam of light is normal to the plane of the molecule. When the electric vector of polarized light was made normal to the plane of the molecule, a new band was found at $\lambda = 5250 \text{ \AA.}$ This can only be interpreted on the assumption that there is a conjugation between the

molecules, which are face to face in the crystal (32), and that the absorption is a result of this conjugation in the z direction.

Far more extensive and instructive are Scheibe's studies of pseudoisocyanine. This substance, in very dilute aqueous solution, shows two bands similar to those which in the case of cyanine crystals we have previously attributed to the x and y directions (the y absorption being apparently intensified in the dimeric form of the substance). When the solutions are made more concentrated, a new intense and narrow band appears at a longer wave length, as shown in figure 24. The appearance of this band, which has no counterpart in the whole field of color chemistry, accompanies the formation of giant molecules. These Scheibe considers as

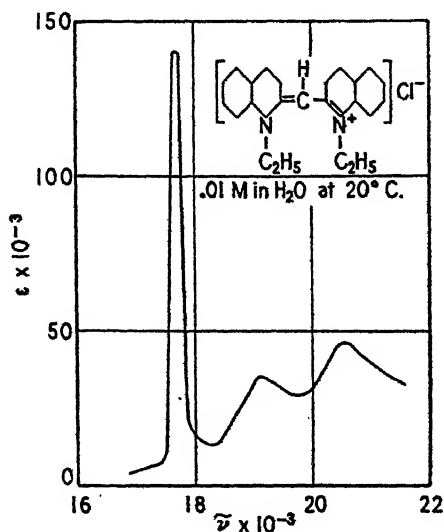


FIG. 24. Fluorescence band of pseudoisocyanine

long threads whose length is normal to the plane of the individual molecules. By various methods of orientation of these threads, together with a study of the fluorescence, he shows that the absorption and reëmission of the narrow band are characterized by an electric vector along the thread, or, as we should say, it is a z band. As Scheibe says "in the process of polymerization the molecules lie flat one to another and there occurs a fusion of certain electrons into a new system, causing the new band. These electrons absorb only light with an electric vector normal to the aromatic plane."

It is also interesting to note that this is the only type of substance, as far as we know, whose fluorescent band coincides in position and half-width with the absorption band.

We believe that the extraordinary narrowness of this z band is to be explained by considerations entirely similar to those that we have used in connection with the polyphenyls. The resonance normal to the planes of the individual molecules must be at the expense of the ordinary resonances of those molecules. Let us assume that polymers containing only a few molecules have an absorption in the z direction that is too weak to be observed, while the higher polymers all have about the same position of the absorption maximum. Then increasing the length of the thread will change only the intensity of absorption, and the phenomenon is readily understood.

INTERACTION BETWEEN ELECTRONIC AND ATOMIC VIBRATIONS

When a molecule that is at low temperature, and is therefore in the zero state of atomic as well as electronic vibration, absorbs light by passing to a higher electronic state, it may also reach one of the states of higher atomic vibration, the probability of each such transition being roughly determined by the familiar Franck-Condon principle. This gives rise to the structure of an electronic band such as has been illustrated in figure 1. This structure usually shows several bands with a separation of the order of 1000 cm^{-1} . However, in complicated molecules there are many types of vibration of much smaller energy, depending upon the mass and the degree of constraint of the various groups.

Even if these minor vibrations are not excited in the very process of light absorption but are excited almost immediately thereafter, thus making the life of the initial excited state very short, this alone, as we have already seen, will broaden the absorption bands. This broadening will tend to make the structure of bands disappear. We are going to think of the disappearance of structure and the quenching of fluorescence as closely related phenomena.

Every molecule that is excited by light has a finite probability of reëmitting the same kind of light. Every substance therefore must be to a certain extent fluorescent. Nevertheless, under ordinary circumstances this fluorescent light is too faint to observe, except in relatively few substances, and the cases are very rare in which the number of emitted photons is approximately equal to the number absorbed. The reason is that there are usually processes for removing the energy of the excited state which are far more probable, that is, which occur on the average in a much shorter time than the reëmission of light.

We have already pointed out the only case (59) known to us (pseudo-isocyanine) in which the band of reëmission is identical with the band of absorption. Ordinarily the bands of emission have a lowered frequency, owing to the loss of energy of electronic oscillation to the more prominent

atomic vibrations, and sometimes it has been found possible to predict the structure of the fluorescence from that of the absorption band (24). An idea of the very extensive work that is now being done in the field of fluorescence is given by the papers in two symposia, one held in Warsaw in 1936 (35) and one in Oxford in 1938 (44).

In atoms and simple molecules the quenching of fluorescence in the gaseous state usually results from collision with walls or with other gaseous molecules. A similar phenomenon is found occasionally in complex molecules; thus the quenching of the fluorescence of fluorescein ion in solution by various substances has been frequently studied. A similar exchange of energy between two molecules but in the opposite direction has been observed with indigo vapor (54), which fluoresces, but not when exposed to light of 2400–2800 Å. On the addition of aniline vapor, which absorbs in this region, the fluorescence of indigo appears.

However interesting these examples may be, as an extension of phenomena previously found in very simple molecules, we must recognize that the main processes that are responsible for quenching or preventing the fluorescence of substances like the organic dyes are within the molecule itself, and we must inquire how and when an electronic oscillation can transfer its energy to the various possible atomic vibrations in the molecule, which in turn, by contact with other molecules or by emission in the infrared, further dissipate their energy. To such a rapid (10^{-13} to 10^{-14} sec.) transfer of energy we may ascribe both the prevention of fluorescence and the disappearance of structure.

It should be possible from our theory of electronic oscillations, localized along definite axes of the molecule, to obtain an idea of the possibility or probability of these dissipative processes. In fact two rules, which we may subject to a variety of experimental tests, are immediately suggested: (1) A group is more likely to take part in the dissipative processes, which tend to eliminate both fluorescence and structure, if it is of large mass or is held by weak constraints, and thus is capable of vibrations of low energy. (2) However, such a group will not be effective unless it takes part in the resonance which is associated with the particular oscillation that is being excited. It seems probable, moreover, that the group will not be effective unless the extreme resonance formulas, toward which the oscillation tends, would favor a different atomic arrangement, with respect to distance or angle, than exists in the normal state of the molecule.

In any molecule the introduction of fluorine, chlorine, bromine, and iodine atoms has long been known to diminish fluorescence and in the order named. Fluorine has the smallest mass and is most tightly bound, while iodine has the largest mass and is least tightly bound. All four resonate with the benzene ring. Benzene itself has a higher efficiency of

fluorescence than the four phenyl halides and the fluorescence diminishes through the series (41).

Let us now compare the absorption spectra of these substances as shown in figure 25 (42). When we examine the structure of the bands, we see the same effect that we have noted with respect to fluorescence. The structure is nearly gone in chlorobenzene and has disappeared entirely in bromobenzene and iodobenzene.

The nitro group, which is one of the strongest acid chromophores, also is capable of vibrations of low energy. It destroys structure and in nearly all known cases completely eliminates fluorescence.

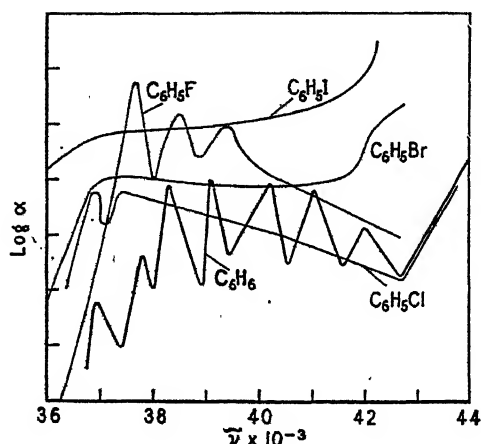


FIG. 25. Absorption curves of benzene and halogenobenzenes

Triphenylmethyl.....
p-Tritolylmethyl.....
p-Trichlorotriphenylmethyl..
p-Triiodotriphenylmethyl....
 Triphenylmethylcarbonic
 acid chloride.....
 Diphenylphenoxymethyl.....
 Biphenylenebiphenylmethyl..

All of these groups that cause a rapid dissipation of the energy of electronic excitation, whether this is manifested by diminution of fluorescence or by diminution of structure, may be likened to loose bolts in some moving part of a machine. They provide a process by which the energy of the system is lost or degraded.

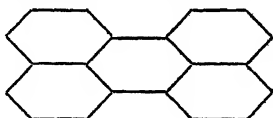
The phenyl group is another example of a radical of large mass held by low constraints, and is a powerful dissipative agent when it becomes a part of the conjugated structure, and is so situated that the resonance in which it participates is associated with that electronic oscillation belonging to

the particular frequency that is being absorbed. These conditions are met in biphenyl. It must, however, be noted that the effect is to be found when such a group as phenyl conjugates with the rest of the system but does not conjugate too strongly. If the conjugation is sufficient to give to the connecting link a large "double-bond character," the constraints of this link become too great to permit vibrations of low energy.

We may illustrate by considering biphenyl and the diphenylpolyenes. In biphenyl the conjugation is not very great; indeed we have seen that even in the long chain of sexiphenyl the absorption band has not reached the visible region, yet the connecting links must have considerable double-bond character, i.e., the distance between the 1 and 1' carbon atoms is 1.48 Å. as against 1.53 Å. for the single carbon-carbon bond (17). In consequence the pronounced structure found for benzene is largely, but not entirely, obliterated, and also biphenyl shows some fluorescence.

When we pass to the diphenylpolyenes there is increased fluorescence (24), and we have seen that they show marked structure. Here we have substances the ordinary formulas of which contain single bonds with heavy groups on either side. Nevertheless, owing to the conjugation, all these bonds acquire a good deal of the character of double bonds. Moreover, it is to be noted that in these molecules of a linear or nearly linear character the interaction between the electronic oscillations and atomic displacements must have only a small component in a transverse direction, in which the vibrations of smallest energy would lie.

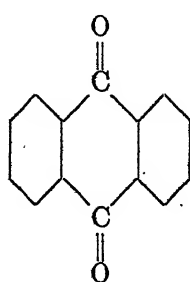
In condensed ring structures, such as perylene,



the planar structure is so rigid that there are no vibrations except of high energy, namely, those which determine the main structure of the electronic bands. If, however, side groups of the kind we have been discussing are substituted in perylene, the structure is not entirely obliterated, but the half-width of each band is greatly increased (15). This effect is greatest for the nitro group, and in 3,10-dinitroperylene the half-width has changed from 125 to 425 Å. If the broadening of the bands is due to the short life of the excited state, it means that the average excited molecule exists for hardly more than 10^{-14} sec. before the electronic energy is partly transferred to the vibration of the nitro group.

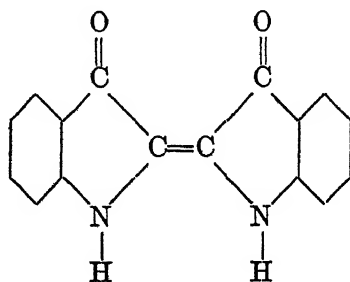
The unsubstituted condensed ring molecules are noted for their powerful fluorescence. Perylene is the only substance that we have found whose vapor fluoresces in ordinary light. The fluorescence of the substituted compounds should be far less pronounced.

Turning now to common dyes, fluorescence is highly restricted. In the *Colour Index* (14), which apparently states the existence of fluorescence whenever it was mentioned in the literature, out of some thirteen hundred substances only about eighty or ninety are listed as fluorescent, and over seventy of these belong to the five following classes: anthraquinone, indigo, azine, xanthene, and acridine dyes. The first two are represented by the structures



Anthraquinone

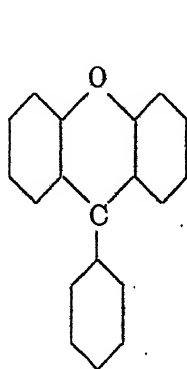
and



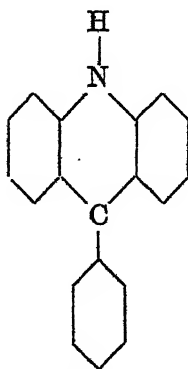
Indigo

The first group resembles the condensed rings we have just discussed. There are no "loose bolts." In the indigos and thioindigos the two halves are separated by a double bond which produces large constraints.

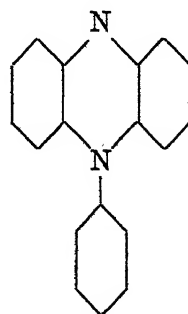
The most remarkable fluorescence is found in the xanthene, acridine, and azine groups, which may be represented, omitting the ionic charge, by the skeleton structures,



Xanthene type



Acridine type



Azine type

Here we have striking confirmation of our rules. While each of them has a rigid structure in the upper part, each has a heavy group not very strongly held,—namely, the lower phenyl group. Furthermore, no matter what substituents we place in this group, they seem to have no effect in diminishing the fluorescence.

We must assume that in xanthene, acridine, and azine dyes the main absorption, and the one corresponding to the observed reëmission as fluorescence, is due to a horizontal oscillation in the upper part of the molecule, as drawn. It is easy to predict that when the γ bands of these substances are examined there will be little corresponding fluorescence, although we have seen one case in which the γ absorption presumably leads to α fluorescence.

Substituents such as OH, $N(CH_3)_2$, $NH(C_2H_5)$, and $N(C_2H_5)_2$ may be introduced into either of the side rings without destroying fluorescence, but not the group $NH(C_6H_5)$, for this introduces a phenyl group in a place where it becomes a part of the oscillating system. Thus rhoduliné violet and methyl heliotrope O differ only in that the $N(CH_3)_2$ group in the former has been replaced by the $NH(C_6H_5)$ group in the latter. The former fluoresces, the latter does not.

Heretofore we have considered the phenomenon of fluorescence only as it appears under ordinary conditions and in ordinary solvents. As a rule fluorescence is far more frequently observed in the ultraviolet than in the visible region. This is probably attributable to increased probability of light emission with increase in the energy of excitation. Even if we confine ourselves to the visible range, the number of fluorescent substances may be greatly increased, and possibly may eventually be extended to include all colored substances, by proper choice of solvent and temperature. We have observed (73) that even such dyes as crystal violet and malachite green show brilliant fluorescence when they are dissolved in glycerol and slightly cooled. The effect in this and similar cases is caused, not primarily by the change of temperature, but by change in the physical nature of the solvent.

Glycerol has often been used as a solvent in experiments on fluorescence, and it has commonly been assumed that the enhanced fluorescence is to be attributed to the high viscosity of the solvent, which would tend to prevent other quenching molecules from reaching the excited molecule. This may be the case when this kind of quenching is responsible for the disappearance of fluorescence. If, however, as we suppose, the most important process in the dissipation of the energy of an electronically excited state is the transfer of energy to atomic vibrations of low energy, within the molecule, a mere change of viscosity cannot be supposed to be effective. However, increasing viscosity usually accompanies an increasing rigidity. Thus glycerol, when it is taken to $-50^\circ C.$ without crystallization, has become a brittle glass, and it would seem that, in such a medium, many of the vibrations of low energy would no longer be possible, because of the constraints imposed by the rigidly held molecules of the solvent. Even in a very fluid solvent similar constraints sometimes are found, if

the molecules of solvent are attached to the solute molecule in such a way as to diminish the freedom of certain vibrations.

ODD MOLECULES

In the paper by Lewis (38) entitled "The Atom and the Molecule," the last section on "The Color of Chemical Compounds" suggests, in old-fashioned phraseology, several of the ideas that we have developed in the present paper. In that paper, odd molecules, that is, molecules with an odd, or unpaired electron, were defined; and it was pointed out that, except for nitric oxide, every known odd molecule was colored. In the twenty-three years that have since elapsed many new molecules of this class have been prepared, and all of them are colored.

The remarkable absorption spectra of the free radicals were obtained in 1911 by Meyer and Wieland (47) and are reproduced in figure 26. We

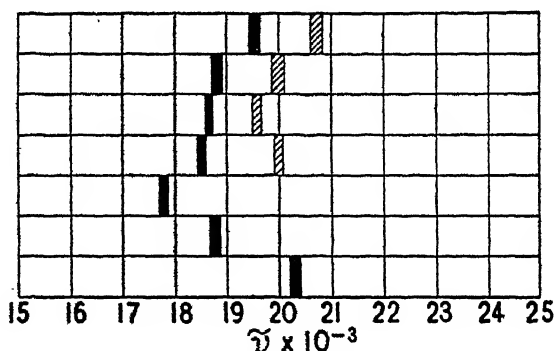


FIG. 26. Absorption spectra of the free radicals

shall comment presently upon the extreme narrowness of the absorption bands.

Examining these spectra, and noting the frequent presence of neighboring pairs of bands in molecules that have been regarded as possessing complete central symmetry in a plane, Lewis (73) concluded that the pair of bands is due to isomers of a new type.

If, using suitable bond distances and angles, the molecule of triphenylmethyl is represented in a plane, the distance between neighboring hydrogen atoms of two benzene rings is only about 0.5 Å. Now we have seen, in reviewing steric effects upon resonance, that the repulsion between two hydrogen atoms as close as this is sufficient to destroy the planarity. If, then, the three benzene rings cannot lie in one plane, but are nevertheless forced to lie near the plane, as a consequence of resonance, there are two possible structures, one symmetrical and the other unsymmetrical.

This would account for the two bands observed in the first four spectra. As a matter of fact Anderson (2) has found, and we have verified, that the right-hand band of triphenylmethyl is double; this may perhaps be due to x and y bands of the unsymmetrical isomer.

When we examine the last three spectra, which are single, we see that, at least in the last two, the molecules are such that the steric influence that would keep the molecule out of a plane is no longer present.

Experiments have been begun, and absorption measurements (73) have been made by Dr. G. T. Seaborg and Mr. O. Goldschmidt, in order to test this isomeric hypothesis. The odd molecule α -naphthyldiphenylmethyl should give four different isomers. Its absorption spectrum shows four very pronounced bands, the first three approximately at 6500, 5900, 5200 Å., and the last still rising near the violet.

If the two bands of triphenylmethyl are due to two substances in tautomeric equilibrium it should be possible to find a change in their relative intensity with the temperature. This effect has not yet been found.

Aside from this phenomenon of multiple bands the most striking characteristic of the spectra of free radicals is the narrowness of the individual bands. The chief band of triphenylmethyl at 5130 Å. has a half-width of hardly more than 100 Å. Such half-widths, however, we have met before in the narrow band of Scheibe (59) and in the individual resolved bands of unsubstituted perylene (15) and of the higher diphenyl polyenes (figure 8). We have attempted to interpret the broadening of the resolved bands of perylene by substituents, but such a small half-width as 100 to 150 Å. can be due to such a variety of causes that we shall not attempt their explanation. It is not due to a short life of the excited molecule, since this life can be measured when the substance is fluorescent and proves to be too long to cause any appreciable broadening.

The characteristic feature of these bands of the free radicals is that they stand alone and are not accompanied by neighboring bands corresponding to excitation of several of the prominent atomic vibrations of which the molecule is capable. This must mean that there is little interaction between the electronic oscillator and any of the atomic oscillators.

When we examine the conditions of resonance in a free radical we find them to be unique. When chlorine is removed from triphenylmethyl chloride, so as to leave an odd electron on the central carbon atom, this electron may pass into the general resonating system and there are nine contributing structures of nearly equal importance: namely, those in which the odd electron is given to the several ortho and para carbon atoms of the three rings. In spite of the fact that the presence of the odd electrons is sufficient to insure wide departure from what we have called an "ideal" molecule, it is to be noted that in each of the contributing structures that

we have just mentioned every atom has zero formal charge. There is therefore no direct relation between the various phases of resonance and the electronic oscillations that we have held responsible for the absorption of light.

The best that we can do at present is to suggest that the presence of an odd electron produces in such molecules a displacement of all electrons from the deep potential troughs of the "ideal" state, that there is thus produced a very mobile electronic cloud located near to, and with its center at, the central carbon atom, and that the oscillations in this cloud have no marked tendency to change the relative distances and angles between the several atoms of the molecule.

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ALKYLATION AND THE ACTION OF ALUMINUM HALIDES ON ALKYL BENZENES

DOROTHY V. NIGHTINGALE

Department of Chemistry, University of Missouri, Columbia, Missouri

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I. INTRODUCTION¹

The principal reactions of pure alkylbenzenes with aluminum chloride may involve dealkylation (dissociation) and alkylation, and either inter- or intra-molecular rearrangement. Depending on its configuration, the dissociated alkyl radical may undergo isomerization, dehydrogenation to form an olefin, or hydrogenation to form a paraffin. It may also alkylate another molecule of the hydrocarbon, or condense with another alkyl radical. Any or all of these reactions may take place, the extent of each depending on such factors as the particular alkylbenzene used, the amount and quality of the metal halide, the time of heating, and the temperature.

Since it appears, as will be shown later, that the initial reaction is dissociation, followed by re-alkylation, a study of the reactions of alkylbenzenes with aluminum chloride should also include consideration of the changes which occur during the alkylation of benzene or its homologs by the Friedel-Crafts procedure or modifications of it. Any theories which account for the formation of alkylbenzenes may also be applicable to the changes which take place when a hydrocarbon reacts with aluminum chloride.

II. ISOMERIZATION AND ORIENTATION

When alkylbenzenes were first prepared by the Friedel-Crafts reaction, some of the early investigators assumed that the radical entering the ring maintained the same configuration that it had in the alkyl halide. This, in spite of the fact that as early as 1879, it was observed that *n*-propyl bromide was converted into isopropyl bromide when warmed with alumi-

¹ Discussions of all the various applications of the Friedel-Crafts reaction are to be found in the reviews by Kranzlein (53), Calloway (15), Linstead (56), and Egloff (23). The booklets *Physical Constants of Mononuclear Aromatic Hydrocarbons* by Egloff and Grosse (22) and *The Physical Constants of the Principal Hydrocarbons* by Doss (20) are very convenient sources of references to alkylbenzenes described in the literature, in addition to their usefulness as handbooks of physical constants.

num chloride at 71°C. for several hours (46). For example, toluene and isobutyl bromide were reported as forming *m*- and *p*-isobutyltoluenes (47). The principal product of this reaction was later identified as the *m*-*tert*-butyltoluene (6), but apparently the para-isomer was overlooked (75).

When the dialkyl homologs of benzene other than dimethylbenzenes are prepared by the Friedel-Crafts procedure, a mixture of meta- and para-isomers is formed with the meta-isomer predominating, rather than an ortho-para mixture as would be expected. In the reaction between the butyl halides and toluene at 0°C., *n*-butyl chloride gave a 75 per cent yield of *m*-*sec*-butyltoluene and a 25 per cent yield of the para-isomer. With isobutyl bromide, the meta-para ratio of *tert*-butyltoluenes was 70:30. Similar results were obtained using ferric chloride as the condensing agent (75).

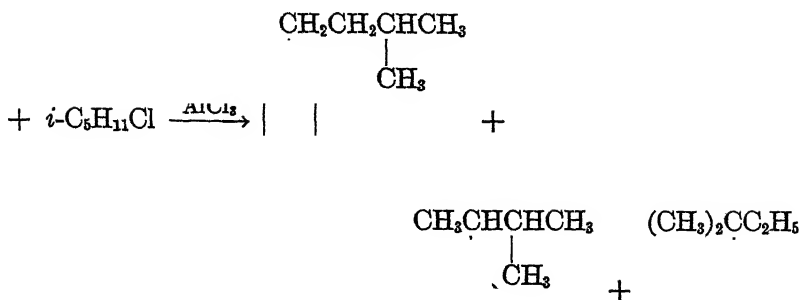
In the syntheses of trialkylbenzenes from benzene, monoalkylbenzenes, or from *m*-dialkylbenzenes by procedures involving the use of aluminum chloride as a catalyst, the principal product has the 1,3,5-configuration rather than the 1,2,4-configuration as would be expected, with the exception of the trimethylbenzenes, and probably the triethylbenzenes under some conditions. In these cases, either the alkyl groups in the meta-position do not exert their usual directing influence, or a 1,2,4-hydrocarbon is first formed and is subsequently rearranged to the 1,3,5-hydrocarbon by the aluminum chloride (61, 72, 81a). In the reaction between an acyl halide and a *m*-dialkylbenzene such as *m*-xylene, the product is a 1,3-dialkyl-4-acylbenzene.

There are conflicting statements in the literature relative to the identity of the propyl radical in the product of the reaction between *n*-propyl halides and benzene. This may be due in part to the different times of heating and different temperatures used by various investigators. At 0°C. the product of the reaction is reported as *n*-propylbenzene, while at higher temperatures a mixture of *n*-propylbenzene and isopropylbenzene results (51, 40).

The reaction between benzene and *n*-propyl formate in the presence of aluminum chloride is noteworthy, for *n*-propylbenzene was reported as the product, even though the reaction mixture stood overnight at room temperature and was subsequently heated to 60°C. (13). *n*-Butyl esters gave *sec*-butylbenzene under similar conditions.

The product from the alkylation of benzene with *n*-octadecyl bromide appears to be *n*-octadecylbenzene. The sulfonamide of the product of the reaction does not depress the melting point of the sulfonamide of *n*-octadecylbenzene prepared by the Wurtz-Fittig reaction or by the reduction of stearophenone (30).

Isoamyl chloride and benzene yielded a mixture of isoamylbenzene, *tert*-amylbenzene, and 2-phenyl-3-methylbutane (52).

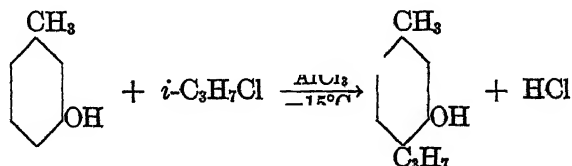


In the furan series, isomerization is even more striking and should be mentioned, even though these data may have no bearing on the alkylation of benzene and its homologs. Methyl 2-furoate and the four butyl chlorides gave methyl 5-*tert*-butyl-2-furoate, but with *n*-amyl chloride and *n*-hexyl chloride there was no isomerization of the alkyl radical (27). When ethyl 5-bromo-2-furoate was alkylated, all alkyl halides containing four or more carbons gave ethyl 4-*tert*-butyl-5-bromo-2-furoate or, in some cases, ethyl-5-*tert*-butyl-2-furoate (27, 29).

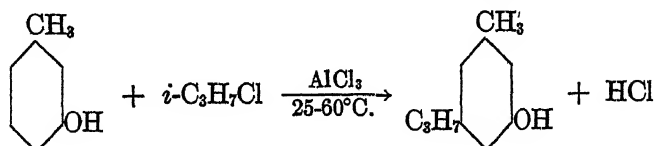
The isomerization of the entering alkyl group is explainable on the basis of Whitmore's theory of intramolecular rearrangements, and the formation of *m*-dialkylbenzenes can be accounted for by Price's mechanism, as will be shown later.

Since the —OH group, small alkyl groups, and halogens are normally ortho-para directing, the products formed when these benzene derivatives are alkylated in the presence of aluminum chloride should have the same orientation as the alkylbenzenes. The 3-methyl-4-*tert*-butylanisole is obtained from *m*-cresyl methyl ether and *tert*-butyl chloride at low temperatures (19), and this is the product which would be expected if the ether group and the methyl group exert their normal directing influence.

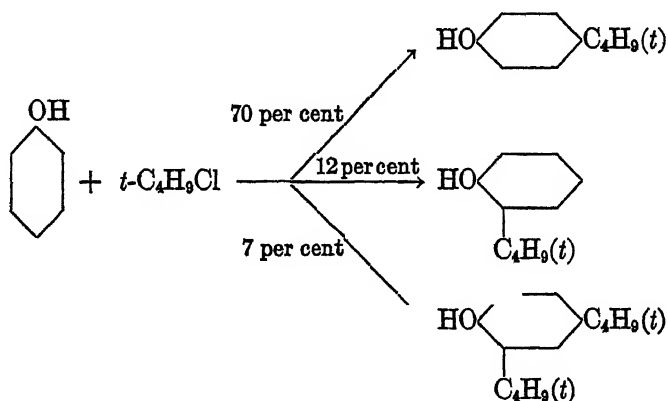
The phenolic group is generally considered as more strongly ortho-para directing than is the methyl group, for in the nitration of *p*-nitrophenol the nitro group enters the nucleus ortho to the hydroxyl group. In the alkylation of *m*-cresol with isopropyl chloride, the hydroxyl group and methyl group should reinforce each other, and the entering isopropyl group would be expected to take the 4-position. Such is the case if the reaction is carried out at -15°C . (31).



If, however, the initial and final temperatures of the reaction are 25° and 60°C., the alkylated phenol has the 1,3,5-configuration.



Phenol itself may be alkylated by means of *tert*-butyl chloride and aluminum chloride. With a mixture of equimolecular quantities of *tert*-butyl chloride and phenol and 1 per cent of aluminum chloride, the products have the normal ortho-para configuration (31).



The initial temperature is 15°C., and is gradually raised to 100°C. *tert*-Butyl alcohol gives similar results (37).

The 1,3-diisopropyl-4-bromobenzene was reported from the reaction of bromobenzene, isopropyl chloride, and aluminum chloride at 0°C. (14).

The methylation of toluene in the presence of aluminum chloride has recently been studied at temperatures ranging from -3° to 106°C. (67a). The data are given in table 1. At the higher temperatures *m*-xylene is the principal product, while at temperatures of -3° to +18°C. the ortho-isomer predominates. In only one other case has *o*-xylene been reported in appreciable quantities from the methylation of toluene (42). The ethylation of toluene and *m*-xylene with ethyl bromide and aluminum chloride at -12° to 0°C. yielded mixtures of ethylated hydrocarbons, the composition of which could not be definitely established.

A comparison of the configuration of the products of the alkylation of these three classes of compounds and the experimental conditions under which they are formed shows clearly that the temperature at which the alkylation is carried out is a primary factor in determining the final position taken by the entering group. The nature of the entering alkyl group may

also be another important factor, if the view is correct that a 1,4- or a 1,2,4-derivative is first formed and is subsequently rearranged.

III. ALKYLATION

Alkylations of benzene or its homologs by any of the procedures other than the Wurtz-Fittig reaction or the Grignard reaction have the following characteristics in common:

The alkyl radical of the alkylating agent may undergo more or less extensive isomerization in the presence of all of the various catalysts which have been studied,—aluminum chloride, ferric chloride, boron fluoride, hydrogen fluoride, sulfuric acid, and zinc chloride.

TABLE 1
Methylation of toluene (67a)

| METHYLATING AGENT + AlCl ₃ | TEMPERATURE | PER CENT XYLENES | | |
|--|-------------|------------------|-----------------|-----------------|
| | | Ortho | Para | Meta |
| | °C. | <i>per cent</i> | <i>per cent</i> | <i>per cent</i> |
| CH ₃ Br..... | -3 | 44.5 | 27.5 | 28.0 |
| CH ₃ Br..... | 5-18 | 45.6 | 28.0 | 26.4 |
| CH ₃ Br*..... | -3 | 49.1 | 20.4 | 30.5 |
| CH ₃ Br..... | +94 | 8.4 | 9.0 | 83.6 |
| CH ₃ Cl..... | 0 | 53.5 | 19.2 | 27.3 |
| CH ₃ Cl..... | 55 | 12.2 | 0.7 | 87.1 |
| CH ₃ Cl..... | 106 | 1.8 | 0.0 | 98.2 |

* Plus AlBr₃.

Aluminum chloride and ferric chloride usually lead to a mixture of *m*- and *p*-dialkylbenzenes with the meta-isomer predominating. With the other catalysts, an ortho-para mixture is obtained.

When the entering group is ethyl, propyl, or larger, the principal trialkylbenzene is generally the 1,3,5-hydrocarbon, if aluminum chloride is the catalyst. In the presence of sulfuric acid the 1,2,4-hydrocarbon is formed. No 1,2,3-trialkylbenzene has been found among these alkylation products.

In spite of their disadvantages, aluminum chloride and anhydrous ferric chloride are the most generally satisfactory catalysts for those alkylations in which their limitations do not prevent their use. In some cases, ferric chloride gives better yields than does aluminum chloride. Aluminum chloride is a more satisfactory catalyst than aluminum bromide.

In the presence of either aluminum chloride or sulfuric acid, the 1,2,4,5-tetraalkylbenzene is formed almost exclusively with the exception of the tetramethylbenzene and possibly the tetraethylbenzene. The tetraalkyl-

benzene fraction from the methylation of benzene or toluene is largely the 1,2,3,5-tetramethylbenzene. The 1,2,3,4-tetraalkylbenzenes have been obtained only by means of the Jacobsen reaction.

No alkylbenzenes have been reported which contain more than three butyl groups or more than four isopropyl groups. Hexa-*n*-propylbenzene has been prepared.

It is well known that in the preparation of monoalkylbenzenes by the Friedel-Crafts procedure, varying amounts of higher alkylbenzenes are formed, owing to the fact that a monoalkylbenzene undergoes substitution more readily than does benzene.

A. The preparation of mono- and di-alkylbenzenes

Within the last few years, a number of procedures have been developed for the alkylation of aromatic hydrocarbons by reagents other than alkyl halides and with catalysts other than aluminum chloride. These procedures are for the most part variations of the Friedel-Crafts reaction.

With aluminum chloride as the catalyst, alkyl halides may be replaced by alcohols (38, 40, 67, 67b), olefins (8, 10, 26), paraffins (32b, 63a), inorganic esters (45), and some organic esters (13, 67b) and ethers (67b). In those cases where the orientations of the di-, tri-, and tetra-alkylbenzenes formed have been determined, their configuration is the same as when the standard Friedel-Crafts procedure is used.

The alkylation of benzene with esters (63) and alcohols (62) may also be accomplished with boron fluoride as the catalyst, and olefins will alkylate with boron fluoride in the presence of sulfuric acid (78). It has been claimed that the use of boron fluoride with sulfuric acid is unnecessary (39), but it has been shown that better yields of alkylbenzenes are obtained when both boron fluoride and sulfuric acid are used (92).

Hydrogen fluoride has been reported as a useful catalytic agent for the alkylation of benzene by olefins and by alkyl halides (76, 14a, 76a).

Most of the investigations of alkylation in the presence of boron fluoride or hydrogen fluoride have been concerned mainly with the formation of mono- and di-alkylbenzenes, and either no attempt was made to prepare trialkylbenzenes, or the fractions containing them were not studied. Trialkylbenzenes formed during alkylation by means of these condensing agents would be expected to have the 1,2,4-configuration, since the dialkylbenzene fraction is an ortho-para mixture with the para-isomer predominating.

A detailed study has been made of the ethylation of benzene, using an excess of ethyl chloride and ethyl bromide with aluminum chloride and aluminum bromide, respectively, under the same experimental conditions, in an effort to compare the efficiency of the two catalysts (88). The aluminum chloride-ethyl chloride combination gave the best yields of

hexaethylbenzene and smaller amounts of lower ethylated benzenes. It is suggested that this may be due to the fact that aluminum bromide is more soluble in the ethyl bromide-hydrocarbon mixture and may bring about the dealkylation of some of the hexaethylbenzene formed.

Anhydrous ferric chloride has not been extensively used as a catalyst for the alkylations of aromatic hydrocarbons, although in those instances where its use is recorded, yields are comparable to those obtained with aluminum chloride.

The yields and proportions of *m*- and *p*-*tert*-butyltoluenes from toluene and *tert*-butyl chloride in the presence of ferric chloride are approximately the same as when aluminum chloride is used (75), and in the reaction between *m*-xylene and cyclohexyl bromide better yields were reported with ferric chloride than with aluminum chloride (4). In these two reactions, both metal chlorides have the same orienting influences. The reaction between *tert*-butyl chloride or isobutyl chloride and toluene in the presence of ferric chloride had first been reported as giving only *p*-*tert*-butyltoluene (9).

The yield of *tert*-butylethylbenzene from ethylbenzene and *tert*-butyl chloride is also said to be better with ferric chloride as the catalyst than with aluminum chloride (5). The orientation of the *tert*-butylethylbenzene was not determined.

The ethylation of benzene by ethyl bromide and ferric chloride gives a mixture of mono-, di-, tri-, and tetra-ethylbenzenes, but no effort was made to determine the orientation of the polyethylbenzenes formed (89).

The alkylation of benzene with propylene and isobutylene in the presence of ferric chloride gave good yields of alkylbenzenes (68). Propylene and benzene in equimolecular ratios with 0.3 mole of ferric chloride at room temperature gave a 91 per cent yield of isopropylbenzene. Isobutylene and benzene under the same conditions gave 89 per cent of *tert*-butylbenzene, and 2 moles of isobutylene with 1 mole of benzene gave a 65 per cent yield of *p*-di-*tert*-butylbenzene. It is of interest that only the *p*-dialkylbenzene was reported from the latter reaction, since *tert*-butyl chloride and toluene in the presence of ferric chloride form a meta-para mixture in the ratio of 70:28 (75). The alkylation of benzene with these olefins and aluminum chloride gave smaller yields of the alkylbenzenes.

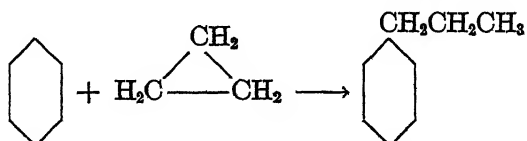
Benzene has been alkylated by ethylene in the presence of hydrogen chloride and beryllium chloride, titanium tetrachloride, zirconium tetrachloride, columbium pentachloride, and tantalum chloride (32a). Temperatures ranged from 75°C. to 200°C. Mixtures of ethylbenzene, diethylbenzene, and the polyethylbenzenes up to hexaethylbenzene were obtained.

Olefins will alkylate benzene in the presence of sulfuric acid in concentrations of 90-96 per cent (39, 39b), as will alcohols in the presence of

70–85 per cent sulfuric acid (48, 58). The dialkylbenzene formed under these conditions is mainly the *para*-isomer.

These procedures can be used only when the isomerization of the entering radical will not lead to an undesired configuration or to a mixture of isomers.

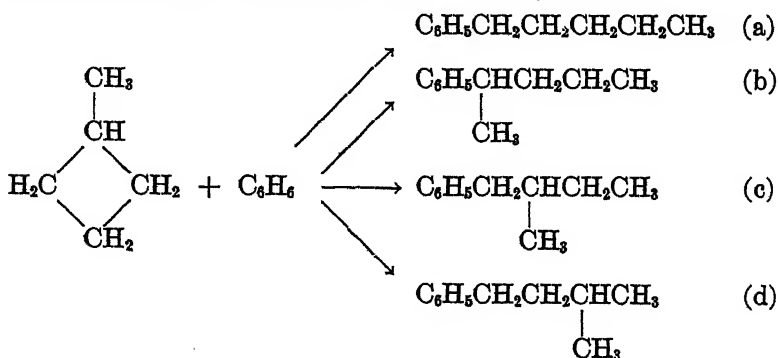
The use of the cycloparaffins and aluminum chloride for the alkylation of benzene has given some interesting results (32). At 0°C. or at 25–30°C., cyclopropane gives *n*-propylbenzene and varying amounts of poly-*n*-propylbenzenes, including hexa-*n*-propylbenzene. There seems to be no doubt as to the identity of this latter hydrocarbon. Cyclopropane and benzene with hydrogen fluoride as a condensing agent also yield *n*-propylbenzene (77).



The formation of *n*-propylbenzene rather than isopropylbenzene from cyclopropane is accounted for as follows (77): "The cyclopropane molecule, being under strain, will be the center of an abnormal electromagnetic field, as indicated by its magnetic susceptibility. This may cause it to add a proton to form a hypothetical and transitory propyl ion. The additional strain may cause the ring to break, and, irrespective of where it breaks, a *n*-propyl positive ion will be formed. The reaction of this ion with benzene will produce *n*-propylbenzene and a proton."

Cyclobutane is reported as reacting readily, presumably to yield *n*-butylbenzene.

Methylcyclobutane could yield four monoamylbenzenes:



A mixture of hydrocarbons was formed, from which isoamylbenzene and 2-phenylpentane were isolated and identified (32). In addition to the products indicated, the reaction could also involve the isomerization of any of these monoamylbenzenes and polyamylbenzenes could also be formed.

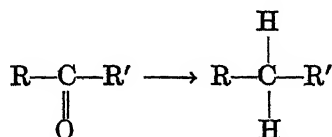
A temperature of 150°C. is required for the reaction of cyclopentane and benzene (32). The products of the reaction are a mixture of amylbenzenes and cyclopentylbenzene. It is probable that *n*-amylbenzene is formed first and is isomerized at the high temperature necessary for the reaction.

Cyclopropane will also alkylate benzene in the presence of sulfuric acid at 0°C. to yield *n*-propylbenzene, but if the temperature is increased to 65°C., the product of the reaction is isopropylbenzene (40). Methylcyclobutane and sulfuric acid at 2–4°C. yield *tert*-amylbenzene (39c).

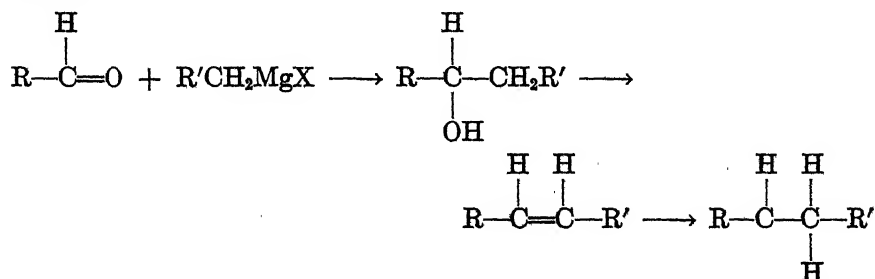
It is suggested that the methylcyclobutane reacts first with the sulfuric acid to form isoamyl acid sulfate. This ester may be converted into *tert*-amyl acid sulfate, which reacts with benzene to form *tert*-amylbenzene (39c). Cyclopropane may form *n*-propyl acid sulfate.

To avoid side reactions as much as possible during the preparation of hydrocarbons by procedures involving the use of aluminum chloride, both the time and temperature of the reaction should be kept at a minimum, and the reaction products should not be left in contact with aluminum chloride any longer than necessary. The value of these precautions is illustrated in the preparation of ethylisopropylbenzene from ethylbenzene and *n*-propyl bromide. The reaction mixture stood at room temperature for 8 days, and the following hydrocarbons were obtained: isopropylbenzene, *m*- and *p*-ethylisopropylbenzenes, *m*-diethylbenzene, and diisopropylbenzene (7).

Hydrocarbons containing normal radicals should be prepared by some other procedure than direct alkylation, with the exception of alkylations with such reagents as cyclopropane. The reduction of a ketone (16) with amalgamated zinc

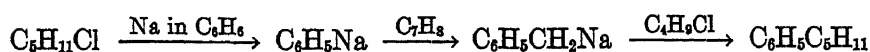


where R is aromatic and R' is aliphatic, is satisfactory if the desired ketone can be readily obtained. Another method makes use of the Grignard reaction



For example, hydrocarbons containing amyl radicals should be prepared by procedures such as these to be certain of the configuration of the amyl radical and to avoid the possibility of mixtures (41, 60).

The Wurtz-Fittig synthesis of hydrocarbons is so well known as to require no comment, but a variation of it should be mentioned. Mono-alkylbenzenes may be obtained in 40 to 70 per cent yields from benzyl sodium and an alkyl halide (60). The preparation of amylbenzene proceeds through these steps



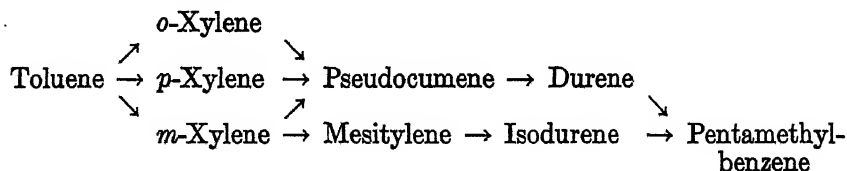
By-products in the preparation of ethylbenzene (yield 42 per cent) from benzyl sodium and methyl iodide are pentene, pentane, and decane formed from the amyl chloride used initially, and some liquids boiling at 174–205°C. Benzyl sodium is recommended as an alkylating agent whenever it can be used, but phenyl sodium and alkyl chlorides “are capable of giving high yields of products other than the expected coupling.”

Typical procedures for the preparation of dialkylbenzenes are those employed in the preparation of *m*- and *p*-di-*n*-propylbenzenes (3) and the meta- and para-forms of *sec*-butyltoluene and *tert*-butyltoluene (75).

B. The preparation of 1,3,5-trialkylbenzenes

Some of the trialkylbenzenes may be synthesized by the Friedel-Crafts procedure, though in some cases the product is a mixture of 1,2,4- and 1,3,5-isomers.

The formation of the various polymethylbenzenes by the methylation of benzene or its homologs is accounted for in this series of reactions (42):



This case and one other (67a) are the only instances in which an appreciable amount of *o*-xylene is reported. The methylation of *m*-xylene at 70–80°C. yielded pseudocumene and mesitylene in the ratio of about 4:1. Pseudocumene was formed almost exclusively from *p*-xylene. Mesitylene gave mostly isodurene and pseudocumene gave durene.

Pseudocumene, mesitylene, durene, and isodurene and other polymethylbenzenes result from the methylation of technical xylene with methyl chloride, or by heating technical xylene with aluminum chloride at 130–

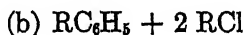
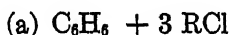
140°C. for 8 to 10 hr. (79). The proportions of the isomers in the crude trimethylbenzene fractions average approximately two parts of the 1,2,4-isomer to one part of the 1,3,5-isomer. In the tetramethylbenzene fractions there is 90 per cent of the 1,2,3,5-hydrocarbon (isodurene) and 10 per cent of the 1,2,4,5-hydrocarbon (durene). When the tetramethylbenzenes undergo the Jacobsen reaction, the product is entirely the 1,2,3,4-tetramethylbenzene.

There is some 1,3-dimethyl-4-ethylbenzene in the product of the reaction between *m*-xylene and ethyl bromide (84), and both 1,2,4-triethylbenzene and 1,3,5-triethylbenzene are listed from ethyl chloride and benzene (49). However, in the synthesis of mesitylene and of 1,3,5-triethylbenzene from benzene and methyl or ethyl alcohol, respectively, no mention is made of the presence of the 1,2,4-isomer (49).

There are also differing statements relative to the products formed in the propylation of benzene (24). Only the 1,3,5-triisopropylbenzene is listed from the reaction of benzene and isopropyl chloride (35). Propylene and benzene give a mixture containing about 75 per cent of 1,3,5-triisopropylbenzene and 25 per cent of the 1,2,4-isomer (8).

Usually the orientation of the trialkylbenzene was determined by oxidizing the hydrocarbon to an acid. In some cases the acid was a dimethylbenzoic acid or a methylphthalic acid, but generally it was trimesic acid or trimellitic acid. In oxidizing a small sample of 1,3,5-hydrocarbon containing a small amount of 1,2,4-isomer, the trimellitic acid could be overlooked during the purification of the trimesic acid. Yields of acids from tetraalkylbenzenes are very poor.

With the various limitations in mind, a variety of 1,3,5-hydrocarbons could be obtained as follows, using aluminum chloride as the condensing agent:



Alcohols (67, 38), olefins (8, 10, 26), some organic esters (13), and some inorganic esters (45) could be substituted for alkyl chlorides with suitable modification of the procedure.

A summary of the reagents used for the preparation of a number of 1,3,5-hydrocarbons as described in the literature is given in table 2.

The 1,3,5-hydrocarbons containing normal radicals, such as tri-*n*-butylbenzene or 1,3-dimethyl-5-*n*-butylbenzene, cannot in general be prepared by procedures involving the use of aluminum chloride.

C. The preparation of 1,2,4-trialkylbenzenes

Prior to 1928, the 1,2,4-hydrocarbons mentioned in the literature, with the exception of pseudocumene, were usually prepared by procedures involving the use of Grignard reagents, or by the reduction of a ketone. Pseudocumene can be obtained from the methylation of benzene with methyl bromide and aluminum chloride at low temperatures (67a), or from *m*-xylene (79).

TABLE 2
Preparation of 1,3,5-trialkylbenzenes

| HYDROCARBON | REAGENTS | REFERENCE |
|--|---|----------------|
| 1,3,5-Trimethylbenzene..... | C ₆ H ₆ , CH ₃ OH | (67) |
| | C ₆ H ₆ , CH ₃ Cl | (42, 79, 67a) |
| 1,3,5-Triethylbenzene..... | C ₆ H ₆ , C ₂ H ₅ Cl | (49, 67a) |
| | C ₆ H ₆ , C ₂ H ₄ | (26) |
| 1-Methyl-3,5-diethylbenzene..... | C ₆ H ₅ CH ₃ , C ₂ H ₄ | (26) |
| 1,3-Dimethyl-5-ethylbenzene..... | <i>m</i> -C ₆ H ₄ (CH ₃) ₂ , C ₂ H ₄ | (26) |
| | <i>m</i> -C ₆ H ₄ (CH ₃) ₂ , C ₂ H ₅ Br | (84) |
| 1,3,5-Triisopropylbenzene.... | C ₆ H ₆ , C ₃ H ₈ | (8) |
| | C ₆ H ₆ , iso-C ₃ H ₇ Cl | (74) |
| 1-Methyl-3,5-diisopropylbenzene..... | Cymene, AlCl ₃ | (72) |
| Tri- <i>tert</i> -butylbenzene..... | C ₆ H ₆ , iso-C ₄ H ₉ Cl | (74) |
| 1,3-Dimethyl-5- <i>tert</i> -butylbenzene..... | C ₆ H ₄ (CH ₃) ₂ , <i>tert</i> -C ₄ H ₉ Cl | (6) |
| | C ₆ H ₄ (CH ₃) ₂ , triisobutyl borate | D.R.P. 184,230 |
| | C ₆ H ₄ (CH ₃) ₂ , <i>tert</i> -C ₄ H ₉ OH | (67b) |
| 1,3,5-Tricyclohexylbenzene... | C ₆ H ₆ , C ₆ H ₁₀ | (18) |
| 1,3-Dimethyl-5-cyclohexylbenzene..... | <i>m</i> -C ₆ H ₄ (CH ₃) ₂ , C ₆ H ₁₀ | (11) |

In 1928 a method was developed for the preparation of alkylbenzenes from benzene and an alcohol in the presence of 70–80 per cent sulfuric acid at 40–70°C. (58). The hydrocarbon and alcohol were added to the acid. Later it was found that the reaction would proceed readily if 80–85 per cent sulfuric acid was added to the mixture of alcohol and hydrocarbon at room temperature (48). By these procedures, the dialkylbenzene formed is mainly para, and the trialkylbenzene has the 1,2,4-orientation.

This method is subject to one of the limitations already mentioned—namely, the isomerization of the alkyl radical during alkylation. *n*-

Alkylbenzenes have not been prepared by this method, and alcohols above the butyl alcohols are likely to give mixtures. For example, 2-pentanol and benzene could yield a mixture of 2-phenylpentane and 3-phenylpentane. The 1,2,4-hydrocarbons containing normal radicals can best be prepared by other methods, such as the reduction of a ketone or by the use of Grignard reagents.

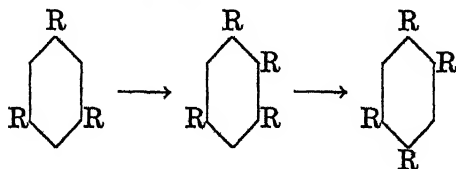
The preparation of 1,2,4-tri-*n*-propylbenzene (3) is a typical procedure by which a tri-*n*-alkylbenzene may be obtained.

D. The tetraalkylbenzenes

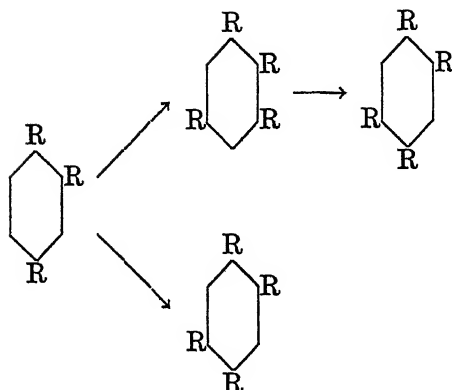
The 1,2,4,5-tetraethylbenzene is the principal product of the reaction between ethyl bromide, benzene, and aluminum chloride at low temperatures (44). A small amount of the 1,2,3,5-isomer is probably formed, but not enough of it could be isolated for positive identification.

The 1,2,4,5-tetraisopropylbenzene is reported from the following reactants: (1) benzene, isopropyl alcohol, and concentrated sulfuric acid (48); (2) benzene, propylene, and concentrated sulfuric acid, aluminum chloride, or hydrogen fluoride (39, 8, 14a); (3) benzene, isopropyl chloride, and aluminum chloride (88). In these reactions, aluminum chloride, hydrogen fluoride, and concentrated sulfuric acid all appear to give the same tetraalkylbenzene. In the case of the tetramethylbenzenes, the 1,2,3,5-hydrocarbon is the principal product.

Since the principal triisopropylbenzene obtained from propylene or isopropyl chloride has the 1,3,5-configuration, the tetraisopropylbenzene formed would be expected to have the 1,2,3,5-configuration as it does in the case of the tetramethylbenzenes, whereas the final product appears to be the symmetrical 1,2,4,5-isomer. If the 1,2,3,5-hydrocarbon is an intermediate product in these alkylations, the formation of the 1,2,4,5-hydrocarbon would require an intramolecular rearrangement involving the migration of an isopropyl group.



In the presence of sulfuric acid as the condensing agent, the trialkylbenzene formed is the 1,2,4-hydrocarbon. The 1,2,4,5-hydrocarbon could be obtained from it by these same changes, or it could be formed directly.



Either type of catalytic agent could lead directly to the symmetrical tetraalkylbenzene through the 1,2,4-hydrocarbon.

It has been reported that a hexapropylbenzene is formed from dipropylbenzene and excess propyl chloride (presumably the normal halide) in the presence of aluminum chloride at room temperature for 40 hr. (88). The melting point of this product is given as 101°C., and the melting point of hexa-*n*-propylbenzene from cyclopropane and benzene is 103°C. (32). Analyses and molecular weight determinations agree with the molecular formula $C_{24}H_{42}$.

In view of the fact that there is more or less isomerization of the *n*-propyl radical during alkylation under these experimental conditions, it would not be surprising if a mixture of poly-*n*-propylbenzenes and poly-isopropylbenzenes were obtained from this reaction. An effort to alkylate 1,2,4,5-tetraisopropylbenzene further with isopropyl chloride in the presence of aluminum chloride at temperatures up to 100°C. gave negative results (32).

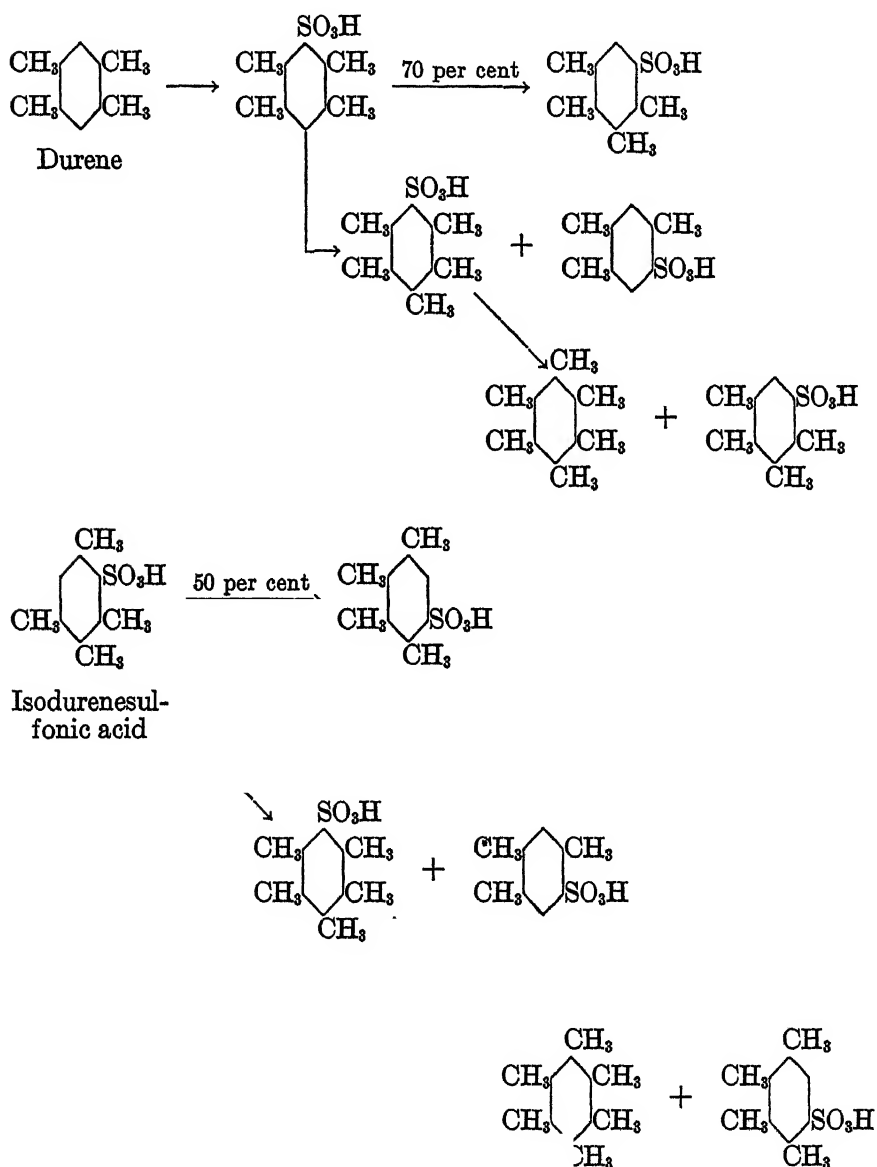
Ethylmesitylene, 3-ethylpseudocumene, and 5-ethylpseudocumene are prepared through the Grignard reaction from the corresponding bromomesitylene or pseudocumene and diethyl sulfate, or by the reduction of the corresponding acetylmesitylene or pseudocumene (80).

While there is apparently no relation between the mechanism of the Jacobsen reaction and the rearrangements with aluminum chloride, it is of interest to compare the two types of reactions. The Jacobsen reaction is the only means by which 1,2,3,4-hydrocarbons have been obtained.

Trimethylbenzenes do not undergo rearrangement by sulfuric acid or other sulfonating agents.

The polymethylbenzenes above the trimethylbenzenes first undergo sulfonation to form a sulfonic acid and then a methyl group migrates either from one molecule to another or to another position in the same molecule. These reactions are illustrated in chart I (61). It should be

noted that in these rearrangements of the polymethylbenzenes, the 1,2,3,4-hydrocarbon is the principal tetraalkylbenzene formed from



durene or isodurene. This hydrocarbon has not been obtained either by direct alkylation or by rearrangements by means of aluminum chloride.

Pentamethylbenzene yields hexamethylbenzene and prehnitenesulfonic acid.

When one of the methyl groups of durene and isodurene is replaced by an ethyl group, the changes are much more complex (81). Both 5-ethylpseudocumene and ethylmesitylenesulfonic acid rearrange to 3-ethylpseudocumene in the main reaction. In secondary reactions, 5-ethylpseudocumene gave prehnitene, 1,3-dimethyl-4-ethylbenzene, and pseudocumene.

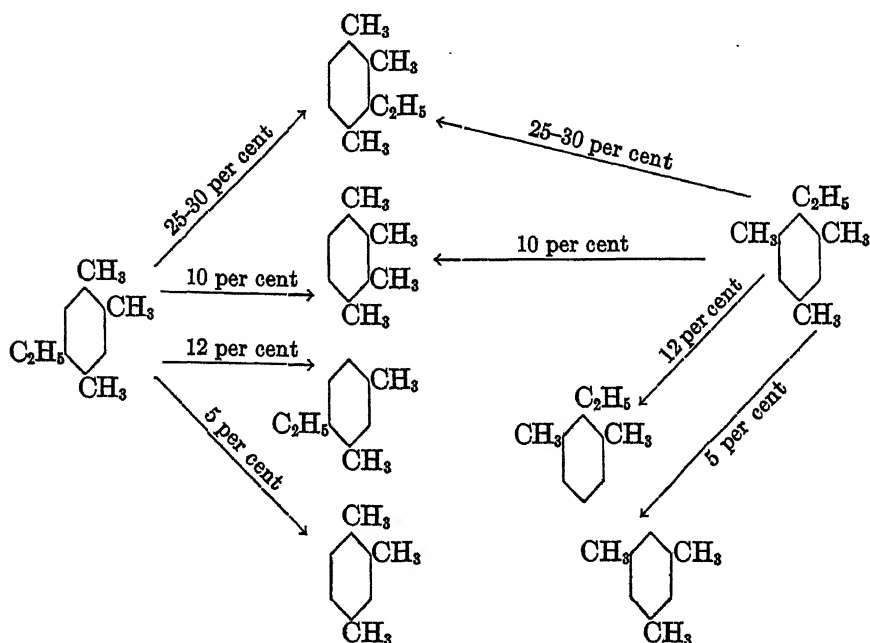


Chart II

Ethylmesitylene gave prehnitene, 1,3-dimethyl-2-ethylbenzene, and mesitylene. These relationships are shown in chart II.

IV. DERIVATIVES OF HYDROCARBONS

The preparation of suitable derivatives of hydrocarbons for purposes of identification is not as simple as it might first appear. The derivatives should be easily obtained in good yields and in pure form from a small amount of hydrocarbon, they should melt without decomposition, and they should give a definite depression of the melting point when mixed with an isomer.

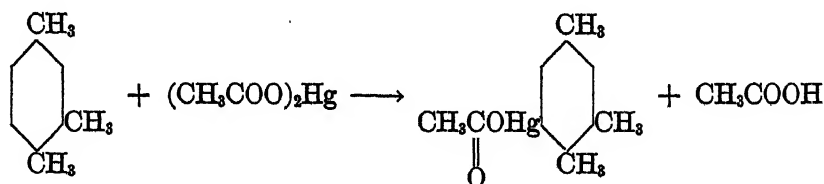
Unfortunately, compounds which are very similar in structure or are isomers often do not give a marked depression of the melting point, par-

ticularly if their melting points are close together. This is especially true of the polyhalogen derivatives of the alkylbenzenes.

Mixtures of polynitro derivatives of isomeric hydrocarbons are more likely to show a definite melting point depression. The preparation of pure polynitro derivatives of some of the alkylbenzenes in good yields is not always readily accomplished, and precautions must be taken to control the temperature of nitration and the composition of the nitrating mixture in order to avoid destruction of any of the alkyl groups, such as large tertiary radicals (4). The trialkylbenzenes in which the radicals are not all the same are likely to yield mixtures of isomeric mono- or di-nitro derivatives, so that complete nitration of the polyalkylbenzenes is carried out whenever possible.

From a 1,2,4-hydrocarbon such as pseudocumene, three mononitro derivatives and three dinitro derivatives are possible. A 1,3,5-hydrocarbon in which all the radicals are the same would yield only one mono- and one di-nitro derivative, but if one radical is different, such as in 1,3-dimethyl-5-ethylbenzene, there are two possible mono- and di-nitro derivatives.

The acetoxymercuri hydrocarbons (82) can be prepared, but the reaction is slow and yields are small.



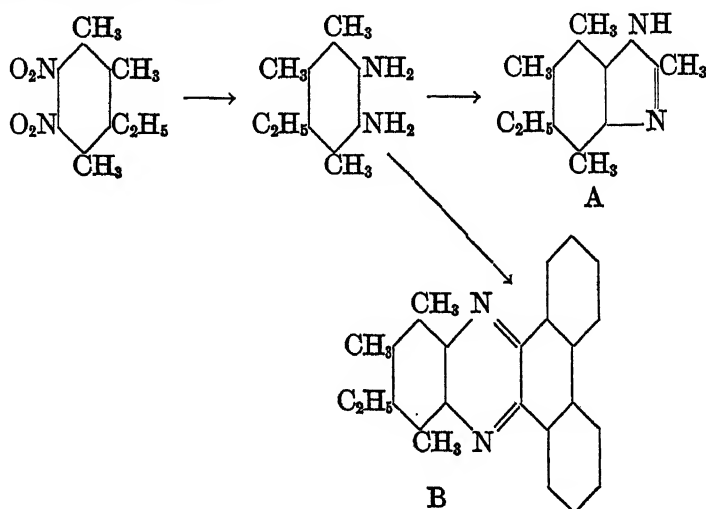
Sulfonation of hydrocarbons and the subsequent conversion of the sulfonic acid to a sulfonamide or substituted amide has been used extensively for purposes of identification, but the reaction is inconvenient for small samples and isomers do not always give satisfactory depressions of the melting point when mixed (81). Concentrated or fuming sulfuric acid causes migration of alkyl groups in alkylbenzenes containing more than three alkyl groups (charts I and II) unless used with great care, and it is possible that radicals larger than methyl might migrate in trialkylbenzenes such as the butyl-*m*-xylenes.

Trialkylbenzenes do not form stable picrates, picrolonates, or styphnates, and the trinitro derivatives of polyalkylbenzenes such as mesitylene and 1,3-dimethyl-5-*tert*-butylbenzene do not form stable addition compounds with naphthalene (19a).

The mono- or di-acetamino derivatives of the monoalkylbenzenes are satisfactory as to ease of preparation and purification and give excellent

depressions of the melting point (40a, 41). The polyalkylbenzenes will give mixtures of isomers corresponding to the nitro derivatives mentioned above.

The dinitro derivatives of 1,2,3,4-tetraalkylbenzenes can be reduced to the corresponding diamines, which undergo ring closure with acetic acid to form a benzamidazole (A) or with phenanthraquinone to form a phenanthrophenazine (B).



No ring closure of this type is possible with meta- or para-diamines.

V. BROMINATION IN THE PRESENCE OF ALUMINUM BROMIDE

If benzene, toluene, or the xylenes are treated with excess bromine containing aluminum bromide (bromine containing about 1 per cent aluminum), the hydrocarbon is completely brominated on the ring. If, however, the hydrocarbon contains radicals larger than methyl, these larger radicals are split off as RBr, replaced by bromine, and the ring is completely brominated (see table 3). The reaction is said to be vigorous even at low temperatures and is quantitative.

The statement that bromination of *m*-xylene in the presence of aluminum chloride gives tetrabromo-*p*-xylene (55) is surprising, since *m*-xylene is more stable in the presence of aluminum chloride than is *p*-xylene, and methyl groups in other hydrocarbons are not affected by bromination under these conditions. No experimental details were given in the abstract.

Bromobenzene and aluminum chloride (17) heated on the water bath for 8 hr. yielded a mixture of benzene, the three dibromobenzenes, 1,3,5-tribromobenzene, and some 1,2,4-isomer. *p*-Dibromobenzene yielded

benzene, bromobenzene, a mixture of dibromobenzenes, and the 1,2,4- and 1,3,5-tribromobenzenes. The tribromobenzene was mostly the 1,3,5-isomer. Chlorobenzene was not affected by aluminum chloride.

Alkylation of bromobenzene with ethylene in the presence of aluminum chloride (8) yielded a mixture of benzene, ethylbenzene, diethylbenzene, and brominated ethylbenzenes.

VI. THE ACTION OF ALUMINUM CHLORIDE ON ALKYL BENZENES

As early as 1885 the investigators of alkylation and of the reactions between aluminum chloride and pure alkylbenzenes concluded that the reaction was reversible, that radicals were removed from a molecule of a hydrocarbon by the metal halide, and that the radical so removed could

TABLE 3

Bromination in the presence of aluminum bromide

| HYDROCARBON | PRODUCT | REFERENCE |
|--|------------------------------|-----------|
| Cymene..... | Pentabromotoluene | (33) |
| 1,4-Dimethyl-2-ethylbenzene..... | Tetrabromo- <i>m</i> -xylene | (10) |
| 1,3-Dimethyl-5- <i>tert</i> -butylbenzene..... | Tetrabromo- <i>m</i> -xylene | (10) |
| 1,2-Dimethyl-4-isopropylbenzene..... | Tetrabromo- <i>o</i> -xylene | (50) |
| 1-Methyl-2-ethyl-3-isopropylbenzene..... | Pentabromotoluene | (50) |
| <i>m</i> -Xylene (with aluminum chloride and bromine)..... | Tetrabromo- <i>p</i> -xylene | (55) |
| Cyclohexylmesitylene..... | Tribromomesitylene | (11) |

alkylate another molecule of the same hydrocarbon or a different hydrocarbon. This early view has proved to be correct.

A survey of the products formed in the syntheses of alkylbenzenes by the Friedel-Crafts procedure and of the products of the reactions of pure aromatic hydrocarbons with aluminum chloride leads to the following generalizations, although data from the various investigators are not entirely comparable, owing to the use of different experimental conditions, and some of the data are conflicting.

The initial reaction is a dissociation of an alkyl radical followed either by re-alkylation of another molecule of the same hydrocarbon or a different hydrocarbon, or by hydrogenation of the alkyl radical to form a saturated hydrocarbon. The source of this hydrogen is not indicated. There is no evidence for the formation of appreciable amounts of olefins.

In suitable cases the dissociated alkyl radical undergoes isomerization.

The formation, either during alkylation or by warming with aluminum chloride, of a mixture of *m*- and *p*-dialkylbenzenes with the meta-isomer

predominating is explainable on the basis of Price's mechanism, as is shown later.

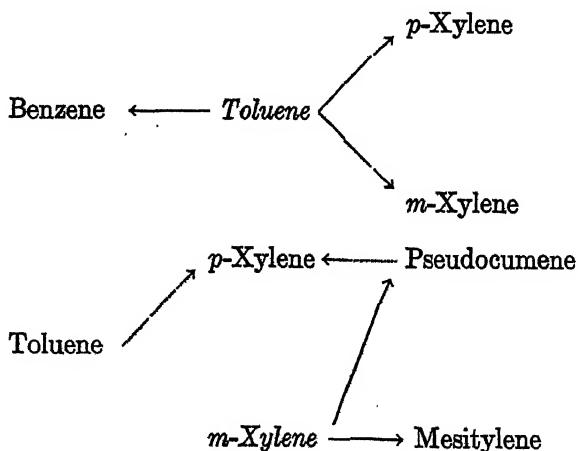
The higher the temperature and the longer the time of heating, the more complex the composition of the mixture becomes, owing to the formation of a variety of benzene homologs in various stages of alkylation, brought about in part by the cleavage of the detached alkyl radicals and some alkylation by the fragments.

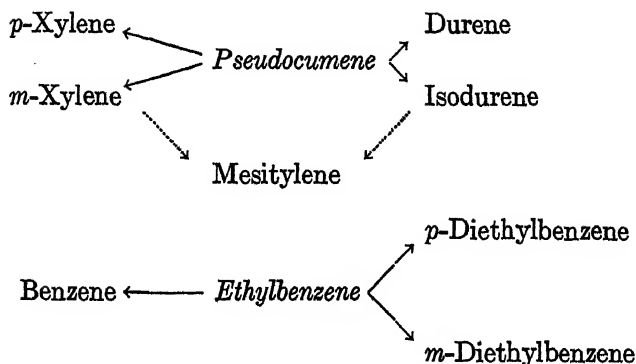
At a given temperature and time of heating, a high concentration of aluminum chloride increases the proportion of dealkylation products, including benzene.

The larger the alkyl radical, the more readily it may be detached from the benzene ring. The bond between the methyl group and the nuclear carbon is the most stable. This is illustrated by the formation of 1-methyl-3,5-diisopropylbenzene from cymene, and of a methyldi-*tert*-butylbenzene, a methyltri-*tert*-butylbenzene and toluene from *p*-*tert*-butyltoluene. Further support for this view is found in the fact that when methylalkylbenzenes are brominated with excess bromine containing aluminum bromide, even at 0°C., all radicals but methyl are lost and the ring is completely brominated (table 3). The 1,2,4-trimethylbenzene appears to be more stable toward aluminum chloride than are other 1,2,4-tri-alkylbenzenes.

The action of aluminum chloride on the methylbenzenes was studied in detail and independently by several groups of investigators, including Friedel and Crafts, who published their results in 1885 (2, 25, 43).

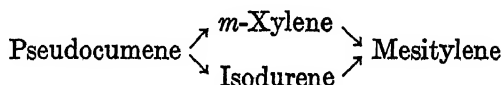
The products of the reaction between the various methylbenzenes and aluminum chloride at their boiling points were accounted for by the following reactions (2):





There was no evidence for an *o*-dialkylbenzene in the reaction products.

It was believed that mesitylene was formed indirectly from pseudocumene



as indicated by the dotted arrows in the diagram. The formation of *p*-xylene from *m*-xylene through toluene and pseudocumene was accounted for in the same way. From ethylbenzene only *m*- and *p*-diethylbenzenes were identified, with the *p*-diethylbenzene predominating, while with toluene the *m*-xylene was the principal dialkylbenzene. The trialkyl fraction from pseudocumene was mainly mesitylene (1).

An effort was made to determine the amounts of the various products in a more extensive study of the reactions of the polymethylbenzenes and aluminum chloride. The results are summarized in table 4.

From the experiments in which quantities of reactants and reaction products are given, it appears that isodurene and durene are formed in proportions of approximately 2:1 except from pseudocumene where the proportions are reversed under some conditions. In the presence of dry hydrogen chloride, the amounts of de-alkylation products are increased. Much of the mesitylene and pseudocumene was unchanged by the aluminum chloride. No effort was made to determine the proportions of 1,2,4- and 1,3,5-isomers in the trialkyl fractions.

When technical xylene is refluxed with aluminum chloride at temperatures of 130–140°C., the crude trimethylbenzene fraction contains pseudocumene and mesitylene in proportions averaging 2:1 (79). The crude tetramethylbenzene fraction consists of approximately 90 per cent isodurene and 10 per cent durene. This would indicate that pseudocumene and isodurene are more stable in the presence of aluminum chloride than are their isomers. No evidence has been found for the presence of any

1,2,3-trimethylbenzene or any 1,2,3,4-tetramethylbenzene among the products of the methylation of benzene or its homologs, or of the demethylation products of penta- and hexa-methylbenzenes, by the action of aluminum chloride.

TABLE 4
The polymethylbenzenes and aluminum chloride (43)

| HYDROCARBON | CONCENTRATION OF AlCl_3 | TEMPERATURE | TIME | PRODUCTS* |
|--|----------------------------------|---------------------|--------------------|--|
| | <i>per cent</i> | $^{\circ}\text{C.}$ | | |
| $\text{C}_6(\text{CH}_3)_6$ | 50 | 190-200 | | $\text{C}_6\text{H}(\text{CH}_3)_5$ } large amounts Durene } Isodurene } |
| | | | | Mesitylene, <i>pseudocumene</i> , <i>m</i> -xylene, toluene, benzene |
| $\text{C}_6(\text{CH}_3)_6$ (+HCl) | 10 | 164 | | Same products but larger amounts of benzene and toluene |
| $\text{C}_6\text{H}(\text{CH}_3)_5$ | 50 | 50-55 | 14 days | Mostly unchanged hydrocarbon, some <i>isodurene</i> , and some hexamethylbenzene |
| $\text{C}_6\text{H}(\text{CH}_3)_5$ (+HCl) | 20 | 100-110 | Sealed tube; 4 hr. | <i>Isodurene</i> and some durene |
| Pseudocumene..... | 12 | 169 | | Benzene, toluene, <i>m</i> - and <i>p</i> -xylenes, durene, <i>isodurene</i> |
| Pseudocumene..... | 10 | 15-25 | 8 weeks | Much durene; no mention of <i>isodurene</i> |
| Pseudocumene (+HCl) .. | 10 | 150-160 | 6 hr. | Benzene, toluene, <i>m</i> -xylene, mesitylene, <i>durene</i> , <i>isodurene</i> |
| Mesitylene (+HCl) | 10 | 150-160 | | Benzene, toluene, <i>m</i> -xylene, durene, <i>isodurene</i> |
| <i>m</i> -Xylene..... | 20 | 139 | | Toluene, <i>pseudocumene</i> , mesitylene, durene |

* The principal isomer is given in italics.

The proportions of the tetraalkyl isomers and trialkyl isomers formed in these experiments are about the same as for the methylation of benzene with methyl chloride (42).

No detailed study has been made of the action of aluminum chloride on pure tetraalkylbenzenes. The tetramethylbenzenes are only mentioned as yielding trimethylbenzenes and xylenes (25) or lower methylated benzenes (43).

The action of aluminum chloride on several alkylbenzenes at 100°C. or over (36) is summarized in table 5.

With regard to the identity of the propyl radical in the reaction products from *n*-propylbenzene, it is maintained that di-*n*-propylbenzenes are obtained along with unchanged *n*-propylbenzene. To substantiate this view, strontium and barium salts of the sulfonic acids and the sulfamides of the reaction products were prepared and this statement made: "These compounds agree with those described by Spica and R. Meyer as characteristic of *n*-propylbenzene." No mention is made of melting points of mixtures of derivatives of any of the reaction products from *n*-propylbenzene with a derivative of an authentic sample of *n*-propylbenzene or of isopropylbenzene.

To determine the effect of aluminum chloride on the xylenes under the experimental conditions for their formation, the three isomers were

TABLE 5
Alkylbenzenes and aluminum chloride (36)

| ALKYLBENZENE | TIME | TEMPERATURE | PRODUCTS IN ADDITION TO BENZENE |
|--|-------|-------------|---|
| | hours | °C. | |
| <i>o</i> - and <i>p</i> -xylenes | 5 | | Mostly <i>m</i> -xylene, pseudocumene, mesitylene |
| <i>m</i> -Xylene | | | Toluene, mesitylene, pseudocumene |
| Ethylbenzene | 10 | 100 | <i>m</i> - and <i>p</i> -diethylbenzenes, triethylbenzene |
| Isopropylbenzene | 4-6 | 100-150 | Propane, <i>m</i> - and <i>p</i> -diisopropylbenzenes |
| <i>n</i> -Propylbenzene | 6 | 100 | <i>m</i> - and <i>p</i> -di- <i>n</i> -propylbenzenes |
| <i>n</i> -Butylbenzene | 5 | | <i>m</i> - and <i>p</i> -dibutylbenzenes |

warmed with aluminum chloride at 55°C. for 10 min. while hydrogen chloride was passed through the mixture (67a). The *o*-xylene yielded 18.7 per cent *m*-xylene and 81.6 per cent unchanged *o*-xylene. The *p*-xylene yielded 0.6 per cent *o*-xylene, 37.1 per cent unchanged *p*-xylene, and 64.3 per cent *m*-xylene. Under these conditions the ortho-isomer is more stable toward aluminum chloride than is the para-isomer.

The action of aluminum chloride on cymene has been carefully studied at temperatures from 60-150°C. and with varying amounts of aluminum chloride (72). Propane, diisopropyl, benzene, toluene, *m*-xylene, and 1-methyl-3,5-diisopropylbenzene were isolated from the reaction products. There was some evidence that small amounts of *p*-xylene and some 1,2,4-hydrocarbon were present, but they could not be isolated.

At the higher temperatures the amount of propane and the amount of the fractions boiling below 145°C. increased, but the amount of trialkylbenzene fraction remained nearly constant.

In another series of experiments, carried out under these same experimental conditions but with amounts of aluminum chloride varying from 10 to 50 per cent, the benzene fraction increased with increasing amounts of aluminum chloride and the toluene fraction decreased.

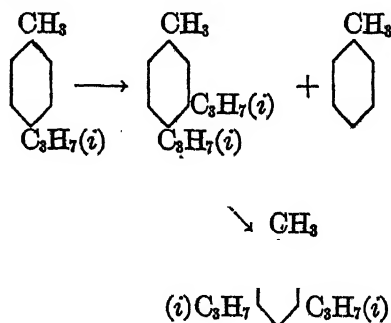
TABLE 6
p-tert-Butyltoluene and cymene with aluminum chloride (54)

| | <i>p</i> -tert-BUTYLTOLUENE | | <i>p</i> -CYMENE | |
|---------------------------------|-----------------------------|----------|------------------|----------|
| | Grams | Per cent | Grams | Per cent |
| Total amount of hydrocarbon.. | 150* | | 50 | |
| Total reaction time, hours.... | 5 | | 240 | |
| Temperature, °C..... | 20-35 | | 20-35 | |
| Unchanged hydrocarbon..... | 27.5 | 18.4 | 18 | 36 |
| Gas..... | 27.5 | 18.4† | | |
| Benzene..... | | | 2 | 4 |
| Toluene..... | 43 | 29.8 | 8 | 16 |
| Xylenes..... | | | | |
| Disubstituted toluene..... | 10.8 | 7.2 | 11 | 22 |
| Trisubstituted toluene..... | 9.1 | 6 | | |
| Higher fractions and residue... | 31.6 | 21.3 | 7.6 | 15.2 |

* Three runs of 50 g. of hydrocarbon and 44.5 g. of aluminum chloride.

† Isobutane.

It is suggested that 1-methyl-3,4-diisopropylbenzene may be formed first and then rearranged to the 1,3,5-isomer.



The 1,3,5-hydrocarbon was oxidized to trimesic acid. There was some qualitative evidence for the presence of trimellitic acid, but none of it could be isolated.

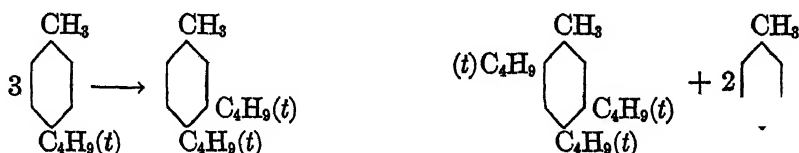
In another investigation, both cymene and *p*-tert-butyltoluene were subjected to the action of aluminum chloride under carefully controlled conditions (54). The results are summarized in table 6.

Analyses and molecular weight determinations of the trialkylbenzene

fraction corresponded to a dibutyltoluene. Nitration did not yield a pure trinitro derivative, and oxidation products were indefinite. The 1,3,4-configuration is suggested for this methyl dibutylbenzene, even though the 1,3,5-configuration is more probable.

Oxidation products of the tetraalkylbenzene fraction from *p*-*tert*-butyltoluene indicate that this hydrocarbon has the 1,2,4,5-configuration. In this connection it should be noted that the tetramethylbenzene formed during the methylation of commercial xylene is largely the 1,2,3,5-hydrocarbon.

In conformity with the suggested configurations, the formation of the principal products isolated could be accounted for as follows:



The products from cymene and aluminum chloride were the same as those reported previously. The oxidation of the diisopropyltoluene with nitric acid yielded 5-methylisophthalic acid. It is of interest to note that no propane, and apparently no tetraalkylbenzene, was obtained from cymene, and no *m*-dialkylbenzene was reported from either cymene or *p*-*tert*-butyltoluene. There was no evidence to indicate the formation of olefins from either cymene or *p*-*tert*-butyltoluene.

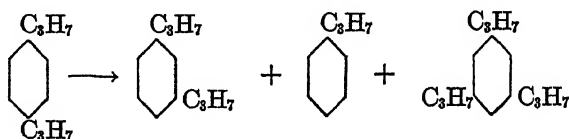
The formation of a tetraalkylbenzene from *p*-*tert*-butyltoluene and not from cymene may imply that the larger radicals such as *tert*-butyl form the more highly alkylated benzenes more readily than do the smaller radicals. The percentage of toluene is correspondingly higher. In this case, there was ample opportunity for the formation of polyalkylated benzenes from cymene, for the time of the reaction was 240 hr. as compared with 5 hr. for *p*-*tert*-butyltoluene.

Cumene heated with aluminum chloride at 150°C. gave a 2.7 per cent yield of toluene and 26.5 per cent yield of xylenes (59). This is attributed to the decomposition of the isopropyl group.

The reaction between the *m*- and *p*-*di-n*-propylbenzenes and the 1,2,4-tri-*n*-propylbenzene in the presence of aluminum chloride has been extensively studied for the purpose of establishing the mechanism for the formation of the reaction products (3).

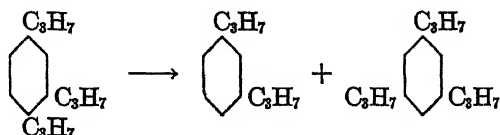
The *m*- and *p*-*di-n*-propylbenzenes were warmed on a steam bath with aluminum chloride for 22 hr. The para-compound gave 11 per cent *n*-propylbenzene, 15 per cent of the *m*-*di-n*-propylbenzene, and 11 per cent of 1,3,5-tri-*n*-propylbenzene, in addition to unchanged hydrocarbon and

residue. The dialkyl fraction from *m*-di-*n*-propylbenzene was mainly unchanged hydrocarbon with small amounts of para-isomer.



A disulfonamide (m.p. 195°C.) of the *m*-di-*n*-propylbenzene and a sulfonamide (m.p. 105°C.) of the *p*-di-*n*-propylbenzene were made. The reaction products from *p*-di-*n*-propylbenzene formed sulfonamides having these same melting points, but there is no record of melting points of mixtures of these derivatives. The conclusions as to the configuration of the migrating propyl group were based on the melting points of the above-mentioned sulfonamides, and on earlier work with the propylbenzenes (36).

The 1,2,4-tri-*n*-propylbenzene and aluminum chloride at 100°C. for 4 hr. yielded approximately 30 per cent of *m*-di-*n*-propylbenzene and 30 per cent of 1,3,5-tri-*n*-propylbenzene in addition to about 10 per cent of higher alkylated benzenes. The trialkyl fraction on oxidation yielded nearly pure trimesic acid.



That a *n*-propyl group, migrating in the presence of aluminum chloride at 100°C., should maintain its identity is questionable. By analogy with the behavior of the *n*-butyl group when 1,3-dimethyl-4-*n*-butylbenzene is warmed with aluminum chloride, the predicted product from 1,2,4-tri-*n*-propylbenzene and aluminum chloride would be 1,3-dimethyl-5-isopropylbenzene. No derivatives were made of the 1,2,4-tri-*n*-propylbenzene or of its rearrangement products.

The principal changes involved when the 1,3-dimethyl-4-butylbenzenes are warmed with aluminum chloride (66, 81a) are shown in chart III, and experimental data are given in table 7. The other products of the reaction are *m*-xylene and, presumably, higher alkylated benzenes. The hydrocarbons boiling above the trialkylbenzenes would not yield a fraction of constant boiling point.

The formation of the by-products would involve the dealkylation of one hydrocarbon molecule and alkylation of another by the detached radical. The 1,3-dimethyl-4-*tert*-butylbenzene could yield *m*-xylene and a di-*tert*-butyl-*m*-xylene.

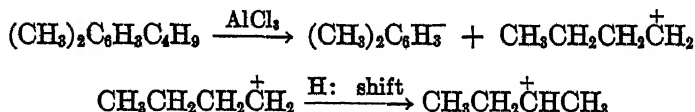
In view of the fact that 1,3,5-hydrocarbons synthesized by the Friedel-Crafts procedure and having radicals up to propyl are reported as containing variable amounts of the 1,2,4-isomer, the question may arise as to whether or not the rearrangement products from 1,3-dimethyl-4-butylbenzenes may contain small amounts of unchanged 1,3,4-hydrocarbon. There is some qualitative evidence for the presence of a small amount of 1,2,4-hydrocarbon in the trialkyl fraction from *p*-cymene (72), but even though relatively large amounts (10 g.) of oxidation product were obtained, not enough of any other acid could be isolated for identification. At the present time there seems to be no satisfactory method for the detection of small amounts of 1,2,4-hydrocarbon in a sample of 1,3,5-hydrocarbon, especially when only small amounts of material are available.

TABLE 7
1,3-Dimethyl-4-butylbenzenes and aluminum chloride (66)

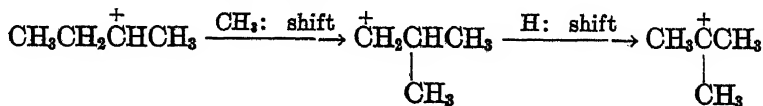
| HYDROCARBON | Amount | AlCl ₃ | TIME | <i>m</i> -XYLENE FRACTION | 1, 3, 5-FRACTION | | | RESIDUE* |
|--|--------|-------------------|-------|---------------------------|------------------|------------|--------------------------------------|----------|
| Name | | | | | Amount | n_D^{20} | Melting point of trinitro derivative | |
| | gms. | gms. | hours | grams | gms. | | °C. | grams |
| 1,3-Dimethyl-4- <i>n</i> -butylbenzene..... | 37 | 8 | 4 | 3.5 | 7 | 1.4928 | 97 | 15.5 |
| 1,3-Dimethyl-4- <i>sec</i> -butylbenzene... | 37 | 8 | 2.5 | 3.5 | 16 | 1.4938 | 113 | 6 |
| 1,3-Dimethyl-4- <i>tert</i> -butylbenzene... | 48 | 10 | 3.25 | 3 | 15 | 1.4935 | 113 | 9 |
| 1,3-Dimethyl-4-isobutylbenzene.... | 50 | 10 | 3 | 4 | | | | 40 |
| 1,3-Dimethyl-4-isobutylbenzene.... | 30 | 7 | 2 | 2 | | | | 26 |

* Includes all fractions which would not yield a constant-boiling cut.

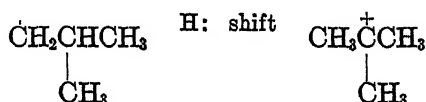
If it may be assumed that the aluminum chloride leads to the formation of butyl ions, the isomerization of the *n*-butyl radical may be interpreted in terms of Whitmore's (91) theory of intramolecular rearrangements, as follows:



The isomerization of the *sec*-butyl radical from 1,3-dimethyl-4-*sec*-butylbenzene could take place similarly:



On this basis, the 1,3-dimethyl-4-isobutylbenzene would be expected to yield readily 1,3-dimethyl-5-*tert*-butylbenzene.



The product of this reaction, however, appears to be a mixture of *m*-xylene and other hydrocarbons.

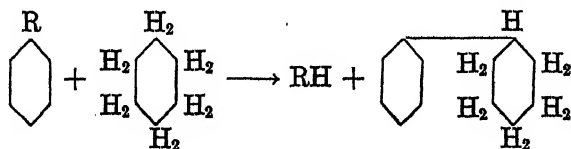
The products from the reaction of alkylbenzenes and some of the cycloparaffins in the presence of aluminum chloride furnish evidence as to the relative stability of some of the different types of alkyl groups.

When an alkylbenzene and either cyclohexane or decahydronaphthalene are warmed with aluminum chloride in the presence of hydrogen chloride

TABLE 8
Alkylbenzenes, cycloparaffins, and aluminum chloride (39a)

| AROMATIC HYDROCARBON USED | PARAFFIN FORMED | | |
|--------------------------------|-----------------|-----------------------|----------------------------|
| | Kind | From cyclohexane | From decahydro-naphthalene |
| | | <i>per cent yield</i> | <i>per cent yield</i> |
| Toluene..... | None | 0 | 0 |
| Ethylbenzene..... | None | 0 | 0 |
| Isopropylbenzene..... | Propane | 33 | 53 |
| <i>sec</i> -Butylbenzene..... | Butane | 35 | 71 |
| <i>tert</i> -Butylbenzene..... | Isobutane | 61 | 94 |
| <i>sec</i> -Amylbenzene..... | Isopentane | 60 | |

at 80°C. for 3 to 4 hr., the alkyl group is split off to yield a paraffin hydrocarbon, the cycloparaffin furnishing the necessary hydrogen (39a).



Other compounds are formed, among them di- and tri-alkylbenzenes and alkylcycloparaffins.

There is a marked difference in the ease with which the alkyl groups are cleaved from the benzene ring, as indicated by the yield of paraffin hydrocarbon (table 8).

Methyl and ethyl groups are not split off under these conditions. Of the two secondary radicals, the isopropyl group is held more firmly, and the tertiary butyl group is more easily detached than is the secondary

butyl group. No experiments are reported in which *n*-alkylbenzenes were used.

The transfer of alkyl groups from one aromatic hydrocarbon molecule to another is illustrated by experiments with approximately 10 per cent solutions of alkylbenzenes in benzene at the boiling point of the solution (12). The data are summarized in table 9.

The results with *p*-cymene are a further indication that the methyl group is more firmly held to the benzene ring than are the larger radicals.

This transfer of alkyl groups to another ring is also illustrated by the alkyl phenols. *p*-*tert*-Butylphenol refluxed with aluminum chloride in benzene solution gave phenol and a 70 per cent yield of *tert*-butylbenzene (83).

TABLE 9
The transfer of alkyl groups (12)

| HYDROCARBON | | AlCl ₃ | BENZENE | PRODUCT | |
|---|----------|-------------------|---------|---------------------------|----------|
| Name | Quantity | | | Name | Quantity |
| | grams | grams | grams | | grams |
| <i>m</i> - and <i>p</i> -xylenes..... | 100 | 10 | 1000 | No toluene | |
| Diethylbenzene..... | 85 | 20 | 850 | Ethylbenzene | 70 |
| Cymene..... | 100 | 20 | 1000 | Toluene | 41 |
| | | | | Isopropylbenzene | 85 |
| Polyisopropylbenzenes..... | 65 | 15 | 650 | Isopropylbenzene | 49 |
| Di- <i>p</i> - <i>tert</i> -butylbenzene..... | 5 | 0.35 | 50 | <i>tert</i> -Butylbenzene | 6.5 |
| Polyamylbenzene..... | 11 | 1 | 110 | <i>tert</i> -Amylbenzene | 3 |

Phenol and 4-(1,1,3,3)-tetramethobutylphenol yielded *p*-*tert*-butylphenol. This latter reaction appears to involve dissociation and cleavage of the octyl group and alkylation by the two four-carbon fragments.

VII. THEORIES

It has long been recognized that the Friedel-Crafts reaction is reversible, and that reactions between a pure alkylbenzene and aluminum chloride may involve both dealkylation and re-alkylation by the detached radical. Most investigators who have studied possible mechanisms to account for variety and types of products formed in a Friedel-Crafts synthesis are agreed that at present no one theory is adequate to explain all of the changes which take place when a hydrocarbon is synthesized by a procedure in which aluminum chloride is used as the catalyst, or when a pure alkylbenzene reacts with aluminum chloride.

From the data assembled by the various investigators and interpreted in

terms of modern concepts of atomic structures and organic reactions, the following general conclusions may be drawn:

Aluminum chloride forms addition compounds with alkyl halides of the type $R:X:AlCl_3$, but these are unstable for the most part, in contrast to the stable addition compounds formed with acyl halides.

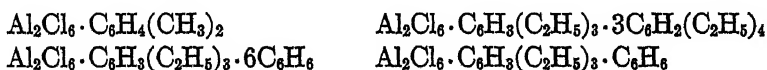
Aluminum chloride and benzene or alkylbenzenes form unstable addition compounds of uncertain composition, which may or may not be essential to the reaction.

These addition compounds may form ternary compounds in which alkylation takes place.

From extensive conductivity studies of the system benzene-ethyl bromide-aluminum bromide, Wertyporoch (88) concludes that "the classical Friedel-Crafts reaction is dependent on the formation of an ionized ternary complex. In the ethyl bromide molecule, the union between C_2H_5 and Br is loosened through salt formation, and likewise the carbon-hydrogen bond in the benzene combined in the cation, and stabilization can take place through the formation of ethylated benzenes with the elimination of hydrogen bromide." Subsequent studies by other investigators have substantiated this view in effect.

It is perhaps unfortunate that in the physicochemical studies of the reaction it was necessary to substitute aluminum bromide or gallium chloride for aluminum chloride in order to obtain satisfactory results, owing to the fact that aluminum chloride is difficultly soluble in aromatic hydrocarbons. The above conclusions are therefore based on the assumption that aluminum chloride behaves similarly.

Gustavson made an extensive study of the nature of addition compounds of aluminum chloride with aromatic hydrocarbons (34). A few typical examples of the many compounds which he reported as isolated are



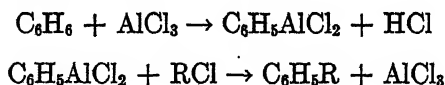
Most of these complexes are described as unstable. From observations of a series of alkylations involving the use of the addition compound $Al_2Cl_6 \cdot C_6H_5(C_2H_5)_3$, he concluded that it and other addition compounds such as $Al_2Cl_6 \cdot C_6(C_2H_5)_6$ and $Al_2Cl_6 \cdot C_6H_4(CH_3)_2$ catalyzed alkylations and were recovered unchanged. These addition compounds were therefore described as having enzyme-like properties. This view was erroneous, and a detailed study of freezing point diagrams of mixtures of aluminum bromide with benzene, toluene, and *p*-xylene has shown that addition compounds of the composition which Gustavson ascribed to them are not formed (57). Aluminum bromide was used rather than aluminum chloride in the freezing point experiments because of the slight solubility of aluminum chloride in

the hydrocarbons. However, the observations as to the formation of addition compounds are of some value as qualitative evidence, for it is generally believed that aluminum halides do form complexes with aromatic hydrocarbons.

According to the recent work of Norris and Rubinstein (67a), toluene and aluminum bromide at room temperature and in the presence of hydrogen bromide form an oily complex the composition of which approximates $\text{Al}_2\text{Br}_6 \cdot 6\text{C}_6\text{H}_5\text{CH}_3$. This complex is easily decomposed and loses toluene in a vacuum, probably forming a more stable complex of the composition $\text{Al}_2\text{Br}_6 \cdot \text{C}_6\text{H}_5\text{CH}_3$. These complexes were not formed in the absence of hydrogen bromide. When aluminum chloride and hydrogen chloride were substituted for the bromides at 80–90°C., a mixture of hydrocarbons resulted and a pure complex could therefore not be obtained. Analyses of the complex indicated that the ratio of Al_2Cl_6 to hydrocarbon was 1:6.

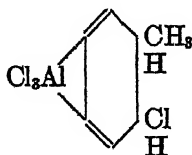
There are little comparable data available to indicate the extent to which the presence of hydrogen halides affects the reactions of alkylbenzenes with aluminum halides. The data cited above indicate that the hydrogen halides promote complex formation, and there is some evidence that hydrogen chloride increases the amounts of some of the dealkylation products.

Early investigators, among them Friedel and Crafts (25), suggested that alkylation proceeded as follows:



Later it was found that organoaluminum compounds of this type are not formed under the experimental conditions for alkylation, and compounds such as $\text{C}_6\text{H}_5\text{AlCl}_2$ do not yield hydrocarbons readily when added to alkyl halides.

Schaarschmidt (71) thought that the aluminum chloride became attached to the nucleus by residual valences, and that the alkyl halide added to this complex to form a dihydrobenzene intermediate product

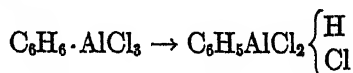


which lost hydrogen chloride and later aluminum chloride.

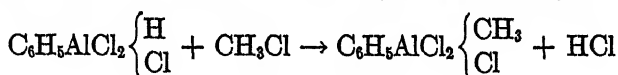
Prins (70) disproved this idea by treating dihydrobenzene with aluminum chloride. The extensive resinification which took place is not observed in a Friedel–Crafts synthesis. Furthermore, if such a dihydrobenzene

complex is formed, it would be expected to take up bromine readily, but on titration with bromine only a small amount was absorbed.

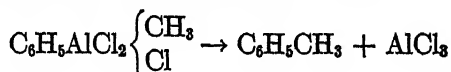
Schröter (73) believed that the hydrocarbon and the aluminum chloride formed a complex which rearranged to form in effect the hydrochloride of an organometallic compound:



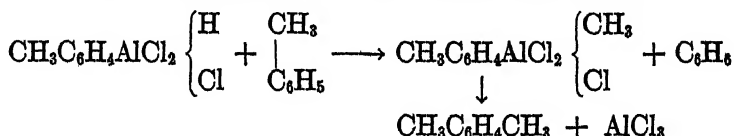
When an alkyl halide was added, the hydrogen was exchanged for a radical,



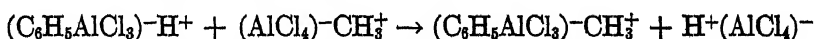
and the double molecule so formed yielded toluene:



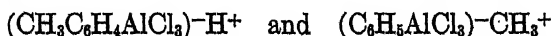
In the same manner, toluene could form benzene and xylene:



Prins expressed the reaction as an interchange of ions. Under the influence of aluminum chloride, benzene could form a phenylchloroaluminic acid. The alkyl halide likewise formed a methylchloroaluminic acid and the two complexes reacted by an interchange of ions:



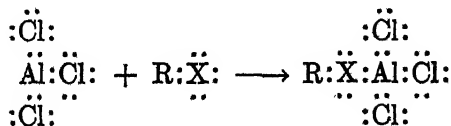
Toluene and aluminum chloride could form two types of complexes



and by an exchange of cations, benzene and xylene were formed.

With the development of the electronic conception of valence and its application to the structures of organic molecules, these earlier theories were interpreted in terms of electronic structures.

The ability of aluminum chloride to form a complex with alkyl halides is thought to be due to the fact that in the aluminum chloride molecule the aluminum atom has only six electrons in its outer shell. It can coördinate with an unshared pair of electrons in another molecule to form a complex.

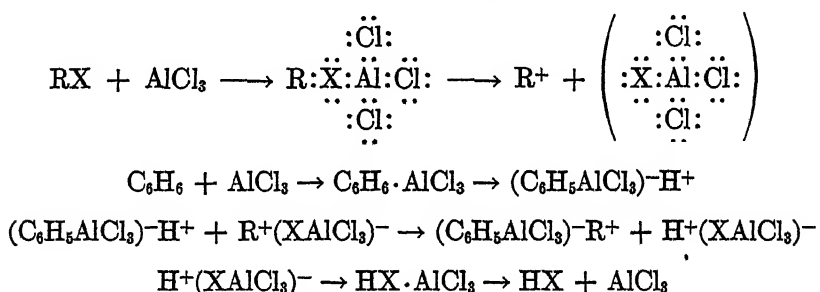


These complexes were expected to have a polar character, and this proved to be true, for solutions of aluminum halides in alkyl halides are conducting.

It would follow by analogy that boron fluoride and boron chloride, which also have an outer shell of six electrons, should catalyze alkylations by means of alkyl halides, but they do not do so (90). It has already been mentioned that boron fluoride does catalyze alkylations by means of alcohols, olefins, and esters. Anhydrous ferric chloride, which has the same electronic configuration in its outer shell as does aluminum chloride, appears to be a satisfactory catalyst for alkylations.

In the reaction between benzyl chloride and toluene in the presence of ferric chloride, there is no evidence for the formation of an addition compound of ferric chloride and the hydrocarbon either formed or used (85). When ferric chloride is added to benzene, there is no evidence of a reaction, but heat is developed when an olefin is added to the mixture (68).

Dougherty (21) expressed the reaction as follows:



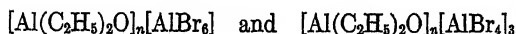
The reaction proceeds toward completion by the formation of the volatile halogen acid. The alkylbenzene so produced may in turn form an ionizing complex which will undergo further alkylation.

In an attempt to find an answer to the many questions which arose in connection with these various theories, Wertyporoch (90, 88, 87) used conductivity measurements in an extensive study of the system hydrocarbon-metal halide-alkyl halide. Aluminum bromide was substituted for aluminum chloride because of the slight solubility of the latter in benzene.

The principal questions which he attempted to answer were: (1) Does aluminum chloride form an addition compound with alkyl halides which may be either an ester of the acid HAlCl_4 or a molecular compound? (2) Is an intermediate product formed with benzene and the aluminum halide, which is independent of the alkyl halide? (3) Do the $\text{AlCl}_3 \cdot \text{RX}$ and $\text{AlCl}_3 \cdot \text{C}_6\text{H}_6$ compounds, if formed, react with each other through an interchange of ions, or do they form a ternary compound?

For purposes of comparison, the behavior of aluminum bromide in ether solution was first investigated. For an approximately 0.5 *M* solution

of aluminum bromide (20 per cent) in ether solution the mol conductivity is = 0.1. The conductivity is thought to be due to the solvate formation of complexes analogous to those formed in solutions of lithium ethyl in zinc diethyl. Wertyporoch regarded the complexes as Al_2Br_6 and $\text{Al}_4\text{Br}_{12}$, changed by solvation into complexes of the type



respectively. These complexes are present in very small concentrations.

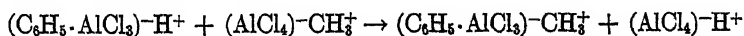
Carefully purified ethyl bromide is practically non-conducting, K being equal to 3×10^{-9} for the specific conductivity. On the addition of aluminum bromide, the conductivity increases with increasing concentrations to about $K = 1.206 \times 10^{-4}$ for a 20 per cent solution of aluminum bromide.

The conducting ternary complex formed when benzene is added to a solution of aluminum bromide in ethyl bromide is precipitated as a dark heavy oil by the addition of a large excess of benzene or saturated hydrocarbon. The supernatant liquid contains hydrogen bromide, but is non-conducting. If the precipitated oil is redissolved in ethyl bromide, its conductivity is unchanged. If aluminum bromide in ethyl bromide is treated with the corresponding amount of hexaethylbenzene instead of with benzene, the solution has the same final conductivity value as when benzene is used.

The question as to the nature of the conducting complexes was studied by means of transference experiments. For a solvate of AlBr_3 , aluminum should concentrate at the cathode. For a solvate of Al_2Br_6 , there should be a migration of aluminum to both anode and cathode, and for $\text{Al}_4\text{Br}_{12}$, three atoms of aluminum should migrate to the anode and one to the cathode. In solutions of aluminum bromide in ethyl bromide, the aluminum accumulates at the anode, indicating that a salt $\text{Al}(\text{AlBr}_4)_3$ is present. This is further confirmed by other transference experiments in the presence of hexaethylbenzene.

From these experimental data Wertyporoch concludes that simple alkyl halides form compounds with aluminum halides in which there is an equilibrium between a "pseudo" salt and an ionized solvate. The fact that stable addition products of the alkyl halide and aluminum bromide cannot be isolated should not be interpreted as disproving the existence of such complexes, since there are many cases in which an unstable intermediate product catalytically active and present in small amounts cannot be isolated.

Since it was not possible to prove directly that the reaction may proceed as an interchange of ions,

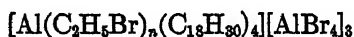


conductivity measurements were used further in an effort to determine if a benzene-aluminum bromide solution has a salt-like character. It is known that the oily complex compounds which result from aluminum bromide and benzene or toluene in the presence of hydrogen bromide conduct well; $K = 10^{-2}$. This holds only for the oil itself. The saturated layer over the oily complex, a very dilute solution of aluminum bromide, is not noticeably conducting.

Benzene has a very small specific conductivity at 25°C.; $K = 1 \times 10^{-13}$. On the addition of aluminum bromide in concentrations up to 20 per cent there is no noticeable increase in conductivity.

The fact that aluminum halides do not form conducting complexes with benzene is interpreted by Wertyporoch as excluding those reaction mechanisms which involve an exchange of ions, but this does not exclude the possible formation of a non-conducting complex between benzene and the aluminum halide.

Transference experiments with a solution of aluminum bromide, ethyl bromide, and benzene show that for approximately four atoms of aluminum, one migrates to the cathode and three to the anode, and that hexaethylbenzene formed or added becomes five times as concentrated at the cathode as at the anode, and also that about four molecules of the hydrocarbon (hexaethylbenzene) and one mole of aluminum migrate to the cathode. This leads to a formula



for the ternary compound, in which aluminum has a coordination number of four and "n" corresponds to a not yet established number of ethyl bromide molecules forming the solvate.

Wertyporoch therefore suggests that the reaction involves first the formation of an ionized complex salt with the aluminum chloride and the alkyl halide. This complex salt may then add to the aromatic hydrocarbon to form a strongly conducting ternary complex in the cation of which the reaction proper takes place. The nuclear carbon-hydrogen bond and the carbon-halogen bonds are weakened in this complex cation. Stabilization takes place with the elimination of the volatile halogen acid and the formation of ethylated benzenes. The manner in which the reaction proceeds in the cation of the postulated ternary compound is as yet unexplained.

Wertyporoch considers the Friedel-Crafts reaction as corresponding to the general scheme of organic reactions such as halogenation or nitration, or molecular rearrangements, which may proceed through the formation of an addition product, decomposition of this addition product, and finally the formation of a stable compound by the elimination of water, halogen acid, etc.

The conductivity studies were extended to include a number of other alkyl chlorides and aluminum chloride, the results of which are given in table 10 (88).

It is suggested that the magnitude of the specific conductivity for chlorocyclohexane and the propyl chlorides as compared with ethyl chloride may be due to the loss of hydrogen chloride from the alkyl halides to form olefins, which form strongly conducting complexes with aluminum chloride.

The changes in conductivity on the addition of the alkylated benzenes,—hexaethylbenzene, propylbenzene, and isopropylbenzene,—to the solutions of the corresponding alkyl chlorides and aluminum chloride paralleled those already described in detail for the aluminum bromide–ethyl bromide–hydrocarbon experiments, except that the final conductivity value was reached more rapidly. The addition of cyclohexane to chlorocyclohexane in the presence of aluminum chloride had no effect on the conductivity.

In a kinetic study of the reaction between *n*-propyl chloride and benzene in the presence of aluminum chloride or gallium chloride, Ulich and Heyne

TABLE 10
Conductivities of alkyl chlorides and aluminum chloride (88)

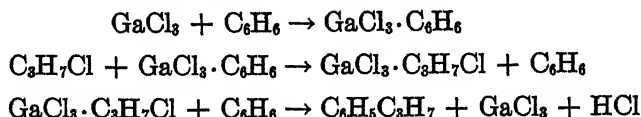
| CHLORIDE | $K \times 10^{-7}$ | | |
|-------------------------|-----------------------|------------------------------|-----------------------------|
| | Specific conductivity | 0.08 mole $AlCl_3$ per liter | 0.2 mole $AlCl_3$ per liter |
| Ethyl chloride..... | 0.03 | 180 | 380 |
| Chlorocyclohexane..... | 0.03 | 650 | 1800 |
| Propyl chloride..... | 0.03 | 3180 | 14400 |
| Isopropyl chloride..... | 0.03 | 3300 | 14000 |

(86) substantiated in effect most of the views of Wertyporoch, and concluded that the reaction involves the formation of the $MCl_3 \cdot C_3H_7Cl$ complex, which is in equilibrium with complexes formed between the metal chloride and benzene and the reaction products.

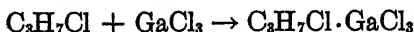
Since aluminum chloride is difficultly soluble, Ulich and Heyne suggested that reaction may proceed slowly on the surface of the solid aluminum chloride. The reaction products dissolve aluminum chloride better than does carbon disulfide, so that a liquid phase results which contains aluminum chloride in the form of a molecular compound with the reaction products. The aluminum chloride so dissolved has a high catalytic activity and may catalyze the reaction with the $AlCl_3 \cdot C_3H_7Cl$ complex.

Gallium chloride proved to be more satisfactory than aluminum chloride in these experiments, because it is readily soluble in carbon disulfide and other solvents of low dielectric constant, forming a homogeneous system. The course of the reaction was followed by measuring at constant pressure the volume of hydrogen chloride evolved. Carbon disulfide was used as

the solvent in all the experiments. These authors represent the reaction as taking place in three steps



but it seems more reasonable that the alkyl halide-gallium chloride addition compound should be formed directly from the two reactants



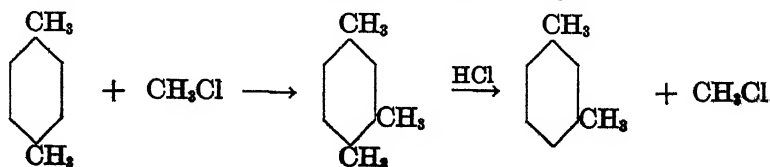
The equilibrium constant was derived for the formation of the complex.

$$\frac{dx}{dt} = K'[\text{GaCl}_3 \cdot \text{C}_3\text{H}_7\text{Cl}][\text{C}_6\text{H}_6]$$

For a large excess of one of the reactants, either benzene or propyl chloride, and a constant amount of gallium chloride, the reaction is of the first order.

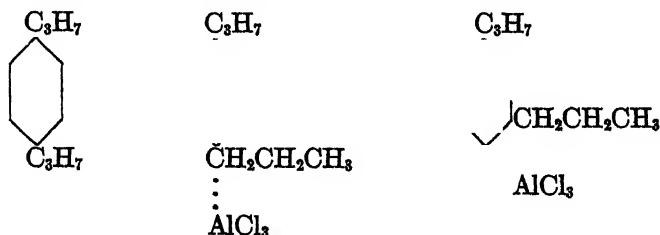
Another physicochemical approach to the problem was made by Fairbrother (24). Powdered aluminum chloride, activated by being exposed to a stream of deuterons, was mixed with inactive aluminum chloride and immediately brought into contact with benzene and *tert*-butyl chloride. A complete interchange of chlorine atoms occurred, the chlorine which formed hydrogen chloride having a radioactivity equal to that of the chlorine which was combined in the final reacting mixture. The radioactivities of the silver chloride from the evolved hydrogen chloride and from the hydrogen chloride obtained from the reaction mixture do not differ by 10 per cent. This leads again to the conclusion that the first step in the reaction is the ionization, by means of aluminum chloride, of the covalent C—Cl bond, with the formation of the negative ion $[\text{AlCl}_4]^-$ and the positive carbonium ion, R^+ . Such a process constitutes "activation" of the aliphatic chloride, in that the ion pair is more reactive in the complex than in the unionized chloride and the final product. A small amount of aluminum chloride will thus serve to activate a large amount of alkyl halide.

To account for the predominance of *m*-dialkylbenzenes in the mixtures of meta- and para-isomers formed in the synthesis of dialkylbenzenes, and for the conversion of a *p*-dialkylbenzene into the meta-isomer, Baddeley and Kenner (3) agreed with Anschütz (2) that a 1,2,4-hydrocarbon could be formed, and subsequently dealkylated to yield the meta-isomer:



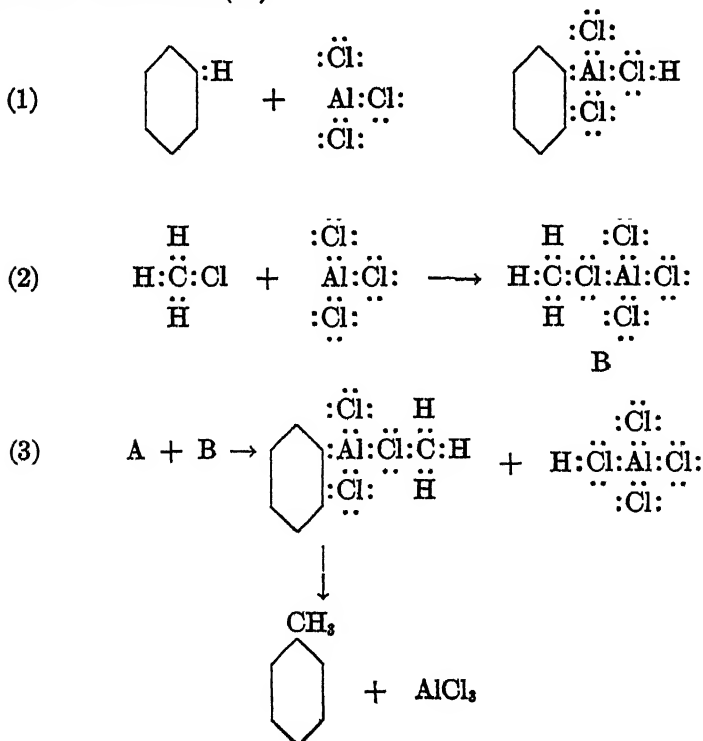
This hypothesis would involve isomerization of the alkyl group in suitable cases, such as the *p*-di-*n*-propylbenzene with which they worked. These investigators concluded that their experimental evidence (no isomerization of the migrating radical) from *p*-di-*n*-propylbenzene and from 1,2,4-tri-*n*-propylbenzene did not substantiate this view.

As an alternative, it was suggested that the rearrangement is a form of the Wagner-Meerwein rearrangement, with the migrant a complex of aluminum chloride and a propyl radical.

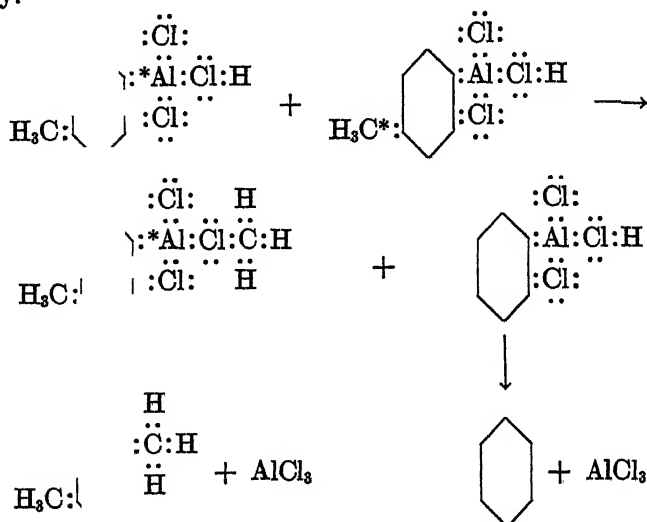


The relative stability of *m*-di-*n*-propylbenzene is accounted for by the assumption that the aluminum chloride may attach itself to the benzene ring para to one of the alkyl groups.

The essentials of some of these theories have been expressed in terms of electronic structures (23).

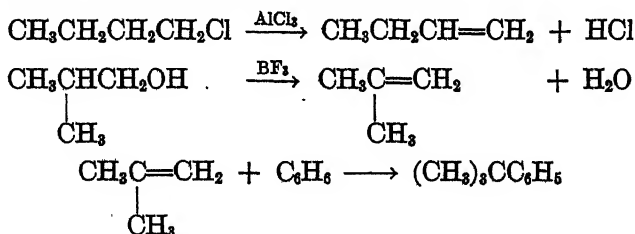


The formation of benzene and *p*-xylene from toluene may occur in the same way.

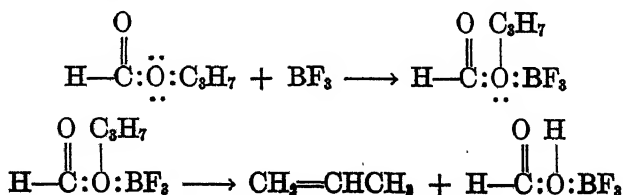


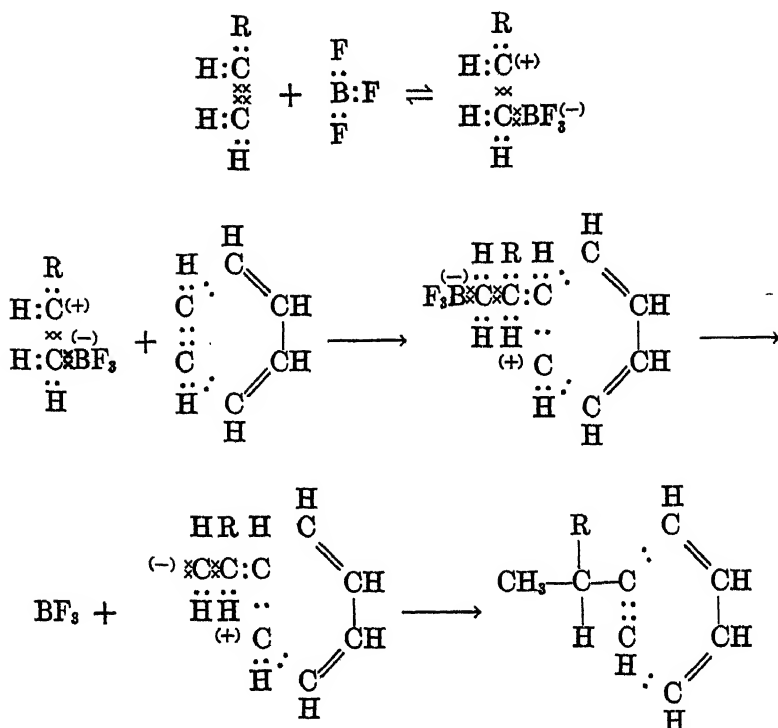
The asterisks correspond to a shift of an electron doublet which makes the methyl group positive relative to the aromatic nucleus.

Alkylation by means of alcohols, esters, and alkyl halides in the presence of aluminum chloride or boron fluoride has usually been interpreted as involving first the formation of an olefin and subsequent addition of the aromatic hydrocarbon to the olefin according to Markownikoff's rule. This accounted for the isomerization of a normal radical to a secondary radical, or of a radical such as isobutyl to tertiary butyl.

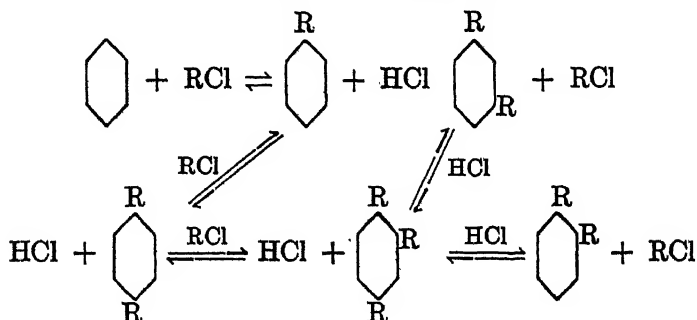


For the alkylation of benzene with *n*-propyl formate in the presence of aluminum chloride, McKenna and Sowa proposed that the boron fluoride coördinated with the oxygen of the ester.





The formation of predominantly meta- as well as para- and ortho-dialkylbenzenes is explained by the following reaction scheme:



The dealkylation of the 1,2,4-hydrocarbon is considered as a substitution of hydrogen in place of an alkyl group, the two radicals in the 1- and 3-positions directing the incoming hydrogen to the 4-position.

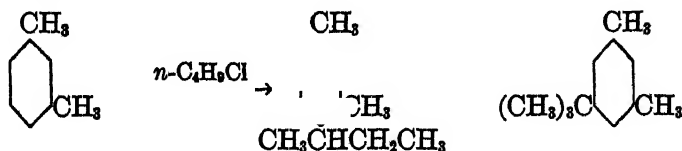
Anschütz and Immendorf (2) had explained the formation of *m*-xylene from pseudocumene in this manner, and Baddeley and Kenner (3) agreed that such an explanation was entirely plausible to account for the formation of *m*-xylene from *p*-xylene, but they discarded the theory.

In support of the view that a 1,2,4-trialkylbenzene is first formed during alkylation and subsequently rearranged to yield finally the 1,3,5-isomer (72, 81a, 61), there is the fact that a 4:1 mixture of pseudocumene and mesitylene results from the methylation of pure *m*-xylene with methyl chloride at 75–80°C. (42). Technical triethylbenzene, presumably prepared from ethyl chloride and benzene, is a mixture of similar composition under some conditions (49). The trimethylbenzenes, and probably the triethylbenzenes, appear to be more stable in the presence of aluminum chloride than are the other alkylbenzenes, and therefore much more of the 1,2,4-hydrocarbon could survive the action of the metal halide, even at temperatures up to 140°C.

The product of the reaction of *n*-propyl formate, benzene, and aluminum chloride is reported as *n*-propylbenzene (13). When *m*-xylene reacts with *n*-propyl formate under the same conditions, the product is 1,3-dimethyl-5-isopropylbenzene (65). Oxidation of the hydrocarbon produces trimesic acid and derivatives of the hydrocarbon do not depress the melting point of derivatives of the hydrocarbon formed from *m*-xylene and isopropyl chloride. These results are explainable on the basis of rearrangement during alkylation, although pure 1,3-dimethyl-4-*n*-propylbenzene is not completely rearranged to 1,3-dimethyl-5-isopropylbenzene even after heating with aluminum chloride at 100°C. for 4 hr. (65).

When the *m*-xylene reacts with *tert*-butyl chloride, the 1,3-dimethyl-5-*tert*-butylbenzene is the principal product. If the assumption is correct that the larger alkyl radicals are more readily detached from the benzene ring than are the smaller radicals, then it would follow that any 1,3-dimethyl-4-*tert*-butylbenzene initially formed would be very largely rearranged to the 1,3,5-hydrocarbon during alkylation.

On the other hand, if this view is correct, the reaction between *m*-xylene and *n*-butyl chloride should lead finally to the 1,3-dimethyl-5-*tert*-butylbenzene:



The 1,3-dimethyl-4-*sec*-butylbenzene would be formed in the first stage of the reaction. The *sec*-butyl radical would dissociate and undergo further isomerization during migration, as is the case when 1,3-dimethyl-4-*sec*-butylbenzene is warmed with aluminum chloride, and the final product of the reaction should be the 5-*tert*-butyl hydrocarbon. Actually the product of this reaction is the 5-*sec*-butyl hydrocarbon.

A summary of some of the data relative to the proportions of the two trialkylbenzenes formed during the alkylation of benzene or *m*-xylene with olefins or alkyl chlorides by means of the Friedel-Crafts reaction is given in table 11.

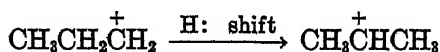
From this qualitative evidence and other data already cited (12, 39a), the inference is that the 1,2,4-trimethyl- and triethyl-benzenes would not be as readily rearranged as are the higher homologs, since the methyl and ethyl radicals are more firmly bound to the benzene ring than are the larger radicals. The data relative to the proportions of the triethyl-benzenes are conflicting, however. The isopropyl group appears to be more easily dissociated, and radicals larger than propyl probably are nearly completely dissociated in the 4-position.

The yields of paraffin hydrocarbons from the reaction between an alkylbenzene and the naphthenes (table 8) lend support to this view.

TABLE 11
Proportions of trialkylbenzenes

| TRIALKYL BENZENES | 1, 2, 4-ISOMER | 1, 3, 5-ISOMER |
|---|-----------------|-----------------|
| | <i>per cent</i> | <i>per cent</i> |
| Trimethylbenzenes (benzene and methyl chloride)..... | 75 | 25 |
| Triethylbenzenes (benzene and ethyl chloride)..... | 70 | 30 |
| Triisopropylbenzenes (benzene and propylene)..... | 25 | 75 |
| Triisopropylbenzene (benzene and isopropyl chloride)... | No evidence | 100 |
| 1,3-Dimethyl-R benzenes, where R is larger than propyl (from olefin or RCl)..... | No evidence | 100 |

The isomerization of alkyl radicals during any of these reactions can be readily explained on the basis of Whitmore's theory of intramolecular rearrangements (91). In the case of the *n*-propyl radical, the changes involved would be



The isomerization of the butyl radicals has already been discussed.

VIII. SUMMARY

From the experimental evidence available at the present time, the following generalizations may be made relative to the mechanism of alkylations by means of aluminum chloride.

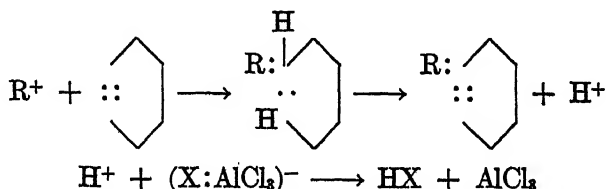
1. The metal halide probably forms a non-conducting, unstable complex with the reacting aromatic hydrocarbon.

2. The aluminum chloride forms a complex, not isolated, with the alkyl

halide of the type $R:X:AlCl_3$. This complex can ionize, yielding a positive carbonium ion and the negative ion $XAlCl_3$.

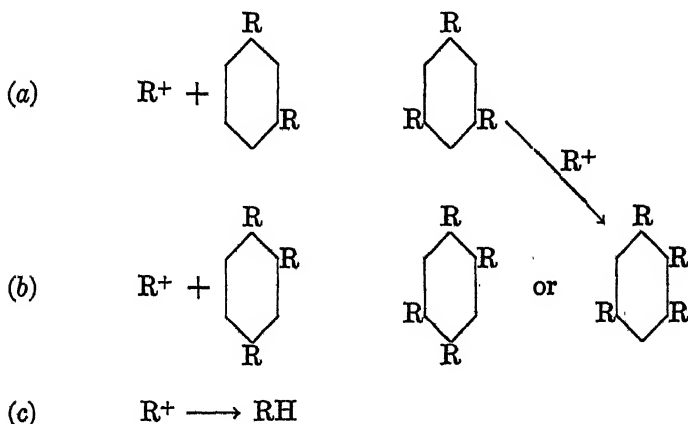


3. Alkylation may then proceed in two ways: (a) The R^+ may co-ordinate with a pair of electrons from a double bond in the benzene ring, followed by the loss of a proton (Price):



(b) The compound $R:X:AlCl_3$ may form a ternary complex with the reacting aromatic hydrocarbon, in which alkylation takes place with the loss of halogen acid (Wertyporoch).

4. The formation of a 1,3,5-hydrocarbon from a 1,2,4-hydrocarbon is explainable on the basis of Price's theory. According to this view, the alkyl radicals in the 2- and 4-positions direct the entering hydrogen to the 1-position, replacing the dissociated alkyl radical. The carbonium ion may then either (a) re-alkylate the benzene ring from which it came to form a 1,3,5-hydrocarbon, or (b) alkylate another molecule of the 1,2,4- or a 1,3,5-hydrocarbon, or (c) be hydrogenated to form an aliphatic hydrocarbon. Reaction (a) is also in accordance with the theory of Smith and Perry.



Again, it must be emphasized that there are much conflicting data in the literature and that no one theory seems adequate to explain these data.

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THE DIELECTRIC CONSTANTS OF POLAR LIQUIDS¹

J. NORTON WILSON

*Gates and Crellin Laboratories of Chemistry, California Institute of Technology,
Pasadena, California*

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A solution to the problem of interpreting the dielectric constants of polar liquids (i.e., liquids whose molecules possess permanent dipole moments) in terms of molecular properties has been sought for a long time. Until recently very little progress had been made; Debye (6) and Fowler (9) had suggested their theory of hindered rotation, but this theory, though it accounts for some of the experimental facts, is not entirely satisfactory. A few years ago, however, a brilliant attack on the problem was made by Onsager (24), who succeeded in developing a theory which appears to account for the dielectric properties of polar liquids in general in a very satisfactory manner. More recently Kirkwood (16) has developed an elegant extension of Onsager's theory.

The major portion of the present review will be devoted to a discussion of Onsager's theory and its application to experiment. This will be preceded, however, by an account of the manner in which Debye's theory of gaseous dielectrics fails when it is applied to polar liquids and solutions. A brief discussion will also be given of the theory of hindered rotation. The derivation of Onsager's equation will then be outlined and a modification suggested which takes the anisotropy of molecular polarizability into account. Following this a qualitative discussion will be given of the specific effects which prevent close agreement between Onsager's theory and experiment, and are to be interpreted as arising largely from the difference between the structures of actual molecules and the model used by Onsager. In this connection mention will be made of Kirkwood's extension of Onsager's theory. Finally, Onsager's equation will be used to calculate dipole moments from the dielectric constants of several polar liquids and solutions. The values obtained will be compared with those calculated from the dielectric constants of polar gases. It will be shown that the sign of the difference between the two values is consistent with the qualitative arguments given in the discussion of Onsager's theory, and

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provides some evidence regarding the nature of the association between polar molecules in liquids.

The dielectric properties of gases can be satisfactorily accounted for in terms of molecular constants by means of the Langevin-Debye equation (4):

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4\pi}{3} \sum_i N_i \left(\alpha_i + \frac{\mu_i^2}{3kT} \right) \quad (1)$$

where ϵ is the dielectric constant, N_i is the number of molecules of the i 'th species present per cubic centimeter, and α_i , μ_i are the corresponding polarizabilities and permanent dipole moments, respectively.

The validity of this equation depends on the assumptions that the applied field E is small enough so that powers of E higher than the first may be neglected, and that in the interior of the gas the effective field acting on a molecule is the so-called Clausius-Mossotti internal field, $\frac{\epsilon + 2}{3} E$. This value of the internal field has been derived rigorously, however, only for cubic crystals and for very dilute gases (20).

It is known experimentally that equation 1 holds quite accurately for non-polar liquids, and that dipole moment values which are fairly consistent with those calculated from the dielectric constants of polar gases can be obtained by the application of the same equation to the dielectric constants of very dilute solutions of polar molecules in non-polar solvents. It has been shown by the careful experiments of Müller (22), however, that the values of the permanent dipole moment obtained from solution measurements depend in a systematic way on the dielectric constant of the solvent; in order to obtain reliable values for the moment of a free polar molecule from studies of the dielectric constant of solutions it is necessary to make measurements using a variety of solvents and to extrapolate to dielectric constant unity. A convenient method for performing this extrapolation has been suggested by Sugden (35).

In concentrated solutions and especially in pure polar liquids equation 1 becomes entirely inapplicable, as may be seen by solving for the dielectric constant ϵ . The expression obtained has as denominator

$$- \frac{4\pi}{3} N \left(\alpha + \frac{\mu^2}{3kT} \right)$$

a quantity which for most polar liquids has a zero in the vicinity of room temperature. In other words, equation 1 predicts for polar liquids a critical temperature analogous to the Curie point, contrary to fact.

A number of empirical equations have been suggested (17, 44, 36) for

the correlation of molecular constants with the dielectric properties of polar liquids and solutions. Of these the most successful is the semi-empirical equation of van Arkel and Snoek (36):

$$\frac{\epsilon}{\epsilon + 2} = \frac{4\pi N}{3} \left(\alpha + \frac{\mu^2}{3kT + CN\mu^2} \right) \quad (2)$$

This equation differs from equation 1 only in the term $CN\mu^2$, which was deliberately introduced to reduce the importance of the dipole orientation term $\mu^2/3kT$. The empirical constant C does not vary greatly from one polar liquid to another (hydrogen-bonding liquids excepted) and is only slightly dependent on temperature; for concentrated solutions of a given polar substance in non-polar solvents it varies little with the nature of solvent. The equation has been discussed at some length by Smyth (30) and by Müller (23), who has also pointed out that the numbers given by van Arkel and Snoek as values of C are in reality values of $3C/4\pi$.

THE THEORY OF RESTRICTED ROTATION

Debye (6) and Fowler (9) have attempted to account for the dielectric properties of polar liquids on the basis of the assumption that a dipole molecule in a liquid is not free to rotate, but rather carries out oscillations about an axis whose direction changes slowly but over short periods of time is fixed by the arrangement of neighboring molecules. When the axis of the dipole is rotated through an angle θ , measured from the momentary axis about which it oscillates, the dipole molecule is assumed to acquire a potential energy $-W \cos \theta$. On the basis of these assumptions and the assumption that the Clausius-Mossotti expression for the internal field will hold in a polar liquid, it is shown that the term $\mu^2/3kT$ in equation 1 must be multiplied by a correction factor $1 - L^2(y)$, where $L(y)$ is the Langevin function $\coth(y) - \frac{1}{y}$ and $y = \frac{W}{kT}$. Using a constant value of W , Debye has been able to account for the differences between gaseous and liquid water with respect to the Kerr effect, molar polarization, and dielectric saturation. No method is known, however, for calculating the energy W theoretically.

If the theory of restricted rotation is to be valid, it appears that the time required for the momentary axis of oscillation of the dipole to become oriented in the applied field should be long compared with the period of the field, which for usual dielectric constant measurements is of the order of 10^{-6} seconds. It has not been shown theoretically that the time required to orient the momentary axis of oscillation is of this order of magnitude; it may well be of the order of the relaxation time of the dielectric, which is known to be about 10^{-12} seconds (7) for most polar liquids.

The theory has been discussed by Van Vleck (39). In his opinion the discontinuities which occur in the dielectric constants and other properties of certain crystals (e.g., hydrogen chloride and hydrogen bromide in the vicinity of 100°K.) may be reasonably explained as due to the cessation of free rotation, but the hindering of free rotation cannot consistently be used to account also for the dielectric properties of these substances at higher temperatures.

A discussion of the theory of free rotation has also been given by Müller (23), who has shown that the energy W may be approximately identified with $\frac{2}{3} CN\mu^2$, where C is the van Arkel and Snoek constant. The theory of Onsager, which will be discussed in the following section, can also be correlated with the van Arkel and Snoek equation but has the advantage of leading to theoretical values of C which agree approximately with experiment.

The objections presented above to the Debye-Fowler theory of restricted rotation should not be considered as implying that hindered rotation does not exist in liquids. It has been pointed out by Kirkwood (16) that the principal difficulty with the theory lies in the assumption of the validity of the Clausius-Mossotti internal field. Kirkwood's extension (16) of Onsager's theory takes the effect of restricted rotation formally into account in a much more satisfactory way.

ONSAGER'S THEORY

It was long ago suggested and has recently been emphasized (24, 38, 39) that the fundamental reason for the failure of equation 1 when applied to polar liquids is the inapplicability of the Clausius-Mossotti internal field. The important advance made by Onsager (24) is the derivation of an alternative expression for the internal field; on this expression he has based the development of a new theory of the dielectric constants of polar liquids. The remaining sections of the present paper will be devoted to a discussion of Onsager's theory and its application.

Onsager represents a polar molecule in a liquid as a point-dipole at the center of a spherical cavity of dielectric constant unity in a homogeneous isotropic continuum of dielectric constant ϵ ; the radius a of the cavity is of the order of the radius of the molecule. For this model it is found by the methods of classical electrostatics that the internal field acting on the dipole may be represented as the resultant of two fields \mathbf{R} and \mathbf{G} : the reaction field \mathbf{R} is caused by polarization of the surrounding medium by the field of the dipole, acts parallel to the instantaneous dipole \mathbf{m} , and exists even in the absence of an applied field; the cavity field \mathbf{G} is caused by and

acts parallel to the applied field \mathbf{E} . These fields are found by straightforward calculation to have the following values²:

$$\mathbf{R} = \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\mathbf{m}}{a^3} \quad (3)$$

$$\mathbf{G} = \frac{3\epsilon}{2\epsilon + 1} \mathbf{E} \quad (4)$$

where \mathbf{m} is a vector representing the instantaneous magnitude and direction of the dipole and a is the radius of the cavity.

The derivation of the Clausius-Mossotti field (5) is formally similar to the foregoing: A spherical surface whose radius is *large* compared to molecular dimensions is imagined to exist in the polarized medium. The field acting on a molecule at the center of this sphere is then considered to be the resultant of two fields: E_1 , the field at that point due to the applied field plus the polarization of the molecules outside the sphere³, and E_2 , the field at that point due to the molecules inside the sphere, except for the molecule under consideration. For a sufficiently dilute gas there will be no molecules except the central one within the sphere, and E_2 will have the value zero. It can also be shown that $E_2 = 0$ in case the dipoles within the sphere are arranged in a cubic lattice. Both these cases lead to the Clausius-Mossotti internal field. For any other case the calculation of E_2 is very difficult; the application of the Debye equation to dilute solutions of polar molecules in non-polar solvents is based on the assumption that E_2 is negligible. That this assumption is invalid is shown by the previously cited experimental work of Müller (22).

The difference between the derivations of the Clausius-Mossotti field and the Onsager field should now be clear: in deriving the former the polarization of the molecule (the material within the sphere) is assumed to have its average rather than its instantaneous value, whereas the Onsager field is derived for the instantaneous orientation of the central molecule. As Onsager pointed out, the value of the reaction field obtained from this calculation is not strictly applicable to any actual liquid because of the simplified molecular model which is used. A more detailed qualitative discussion of this point will be given later.

We may now continue with the development of Onsager's theory.

² All quantities printed in bold-face type are to be considered as vectors. The derivation of equations 3 and 4 is given in an appendix to this paper.

³ Note that G is the field due to the applied field and material outside the sphere when the sphere is empty.

Under the influence of the fields \mathbf{R} and \mathbf{G} the molecule will be polarized so that its dipole moment will be, not the permanent moment μ , but

$$\mathbf{m} = \mu \mathbf{u} + \frac{3\epsilon}{2\epsilon + 1} \alpha \mathbf{E} + \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\alpha}{a^3} \mathbf{m} \quad (5)$$

where \mathbf{u} is a unit vector in the direction of the permanent dipole μ . After this equation is solved for \mathbf{m} , it is easy to calculate the potential energy of the dipole as a function of its orientation in the applied field, and by the use of Boltzmann statistics to evaluate \bar{m}_z , the average moment in the direction of the applied field. The details of this procedure are given in the appendix to the present paper. The equation for the dielectric constant of the liquid is then obtained by the use of a fundamental equation of electrostatics:

$$\bar{P} = \frac{\epsilon - 1}{4\pi} E = N \bar{m}_z \quad (6)$$

In order that the resulting equation shall reduce to the Debye equation for non-polar liquids it is necessary to define the radius a of the cavity by the equation

$$\frac{4\pi}{3} N a^3 = 1 \text{ cm.}^3 \quad (7)$$

It is also convenient to substitute for the polarizability α the index of refraction n , by means of the equation

$$\frac{n^2 - 1}{n^2 + 2} = \frac{4\pi}{3} N \alpha = \frac{\rho}{M} (P_E + P_A) \quad (8)$$

where ρ is the density of the liquid, M is the molecular weight, and P_E and P_A are the so-called electronic and atomic molar polarizabilities, respectively.

Onsager's equation for the dielectric constant of polar liquids, with the usual approximation that powers of E higher than the first are neglected, then assumes its usual form

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)} = \frac{4\pi N}{3} \frac{\mu^2}{3kT} \quad (9)$$

DISCUSSION OF ONSAGER'S THEORY

When the preceding treatment is carried out in detail it is found, after the substitutions given in equations 7 and 8 have been made, that the

value m of the dipole in the liquid in the absence of an applied field is greater than the permanent moment μ by the factor

$$\frac{(n^2 + 2)(2\epsilon + 1)}{3(2\epsilon + n^2)}$$

At 0°C. this factor has the following values⁴: for ethyl bromide, 1.40; ethyl ether, 1.23; chlorobenzene, 1.34. Evidence for the predicted increase in dipole moment is afforded by the influence of the dielectric constant of the solvent on the rate of some chemical reactions of polar solutes (40) and by the fact that the absorption of infrared radiation of the appropriate vibrational frequencies by HCl and HBr is much greater in the pure liquid or in solution than in the vapor (26, 42). The absorption coefficient depends to be sure not on μ but on $(\partial\mu/\partial r)$, where r is the coordinate involved in the vibration; nevertheless the large change in $\partial\mu/\partial r$ suggests that a considerable change has taken place in μ also. In solution, moreover, the Raman frequencies of hydrogen chloride, hydrogen bromide, ammonia, and sulfur dioxide are lower than in the gas phase; the frequency shift seems to depend in a systematic way on the dielectric constant of the solvent (41).

In the original development of Onsager's theory no account was taken of the optical anisotropy of the polar molecule. This is of some importance, since the reaction field R is directed along the axis of the instantaneous dipole of the molecule, and this in turn has its principal component along the axis of the permanent dipole. It is known from measurements of the Kerr effect and of the depolarization of scattered light in polar gases that the polarizability along the dipole axis is in general different from the polarizability averaged over all directions. We may take this fact into account in the following way: We assume that the forces acting on the dipole are given by equations 3 and 4 and take components A and B of the instantaneous dipole m in the directions of E and of the permanent dipole,

⁴ A similar increase in moment on solution of a polar molecule in a liquid has been predicted by Fairbrother (8) on the basis of the concept that the state of a polar molecule may be roughly described as the result of quantum-mechanical resonance between a pure covalent and a pure ionic state. The magnitude of the dipole moment is determined by the extent to which the ionic state contributes to the structure. The ionic state is stabilized in solution by the energy of solvation of a dipole and consequently makes a greater contribution to the state of the molecule in solution than in the vapor. This calculation is essentially the same as that made by Onsager, but is expressed in a different language; it predicts an increase in the dipole moment of the same order of magnitude as does Onsager's theory but may be no more accurate because of the necessarily approximate value of the solvation energy which was used and the approximate nature of the quantum-mechanical variation treatment which was adopted.

i.e., along the unit vector \mathbf{u} . Assume that the polarization produced by forces in the direction of \mathbf{u} may be calculated by use of the polarizability α_1 along the dipole axis, while that produced by forces in the direction of \mathbf{E} may be calculated by use of the average polarizability α . (This is a good approximation, since for fields far from saturation the orientation of the dipole in the field is nearly random.) Proceeding as in equation 5 we obtain

$$\mathbf{m} = A\mathbf{u} + B\mathbf{E} = \mu\mathbf{u} + \frac{3\epsilon}{2\epsilon + 1} \alpha\mathbf{E} + \frac{2(\epsilon - 1)}{(2\epsilon + 1)} \left(A \frac{\alpha_1}{a^3} \mathbf{u} + B \frac{\alpha}{a^3} \mathbf{E} \right) \quad (10)$$

Equating coefficients of \mathbf{u} and \mathbf{E} separately we may solve for A and B , and, substituting for a^3 and α by means of equations 7 and 8, and for α_1 by means of an equation in n_1^2 similar to equation 8, we obtain

$$\mathbf{m} = \frac{(2\epsilon + 1)(n_1^2 + 2)}{3(2\epsilon + n_1^2)} \mu\mathbf{u} + \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2} \alpha\mathbf{E} \quad (11)$$

Proceeding from this point just as in Onsager's original treatment we obtain as our final result

$$\frac{\epsilon - 1}{\epsilon} - \frac{3(n^2 - 1)}{2\epsilon + n^2} = \frac{4\pi N}{9kT} \mu^2 \frac{(2\epsilon + 1)(n_1^2 + 2)^2}{(2\epsilon + n_1^2)^2} \quad (12)$$

A more tedious but more rigorous treatment in which it is assumed that the polarizability ellipsoid of the molecule has components $\alpha_1, \alpha_2, \alpha_3$ to which correspond indices of refraction n_1, n_2, n_3 , and that the permanent dipole μ is parallel to α_1 yields an equation identical with equation 12 except that the term

$$\frac{3(n^2 - 1)}{2\epsilon + n^2}$$

becomes

$$\frac{n_1^2 - 1}{2\epsilon + n_1^2} + \frac{n_2^2 - 1}{2\epsilon + n_2^2} + \frac{n_3^2 - 1}{2\epsilon + n_3^2} \quad (13)$$

The correction 13 is not important for polar liquids at usual temperatures where ϵ is large.

It was realized by Onsager that for several reasons his method of calculation can give only a rough approximation to the value of the reaction field in actual liquids: the treatment of the molecule as a sphere containing a central dipole, the treatment of the environment of the molecule as a homogeneous continuum, the neglect of dielectric saturation in considering the effect of the strong fields in the vicinity of the central dipole, and the arbitrary choice of the value of a , the radius of the cavity, are all obviously approximations.

The reaction field arises chiefly from the polarization of those molecules which are close to the central dipole. At short distances it is certainly not permissible to consider the environment of the central dipole as a continuum, since the amount of polarizable matter contained in a continuum will be greater (by a factor which we shall call β) than the amount contained in the discontinuous medium. The reaction field calculated on the basis of a continuous environment of the central dipole will then be too large by approximately the factor β . The error may be corrected by using a value of a^3 which is greater by a factor β than the average of the cube of the molecular radius. This correction is in fact achieved by the use of the definition of a given in equation 7, since if the molecule is considered to be a rigid body the volume of the cavity is greater than the volume of the molecule by precisely the factor β . We may consider then that the definition of a given in equation 7 brings Onsager's theory into agreement with the dielectric properties of non-polar liquids by correcting for the discontinuous nature of the environment of the molecule. It is not to be expected that this correction will work as well in polar liquids however.

It is difficult to estimate the magnitude and for many molecules even the sign of the error which is introduced into the calculation of the reaction field by the fact that the structure of actual molecules differs from Onsager's model. Departure of the structure of the molecule from agreement with Onsager's model may be expected in the majority of cases to make the true value of the reaction field greater than that calculated by Onsager, since the structure of most polar molecules is such that neighboring dipoles are able to approach the dipole of a given molecule to within distances smaller than $2a$. On the other hand, dielectric saturation effects in the strong fields surrounding a given dipole will, if they occur, be expected to make the true value of the reaction field less than that calculated by Onsager. It is evident that the estimation of the resultant effect of the various errors entering into the calculation of the reaction field is a very difficult matter; no attempt will be made in the present paper to carry out such an estimation. In making applications of Onsager's theory to experimental data it must be borne in mind that a reaction field error exists, and that the error will not be negligible even in very dilute solutions of polar solutes in non-polar solvents.

Disagreement between experiment and Onsager's theory will be expected to arise from still another cause, which we shall call the *association error*. It has been shown by Fuoss (11) that, in solutions of polar substances in non-polar solvents, the attractive forces existing between dipoles will be expected to lead to the formation of aggregates of polar molecules. These aggregates will not be oriented in the applied field in the same manner as

simple dipoles, since each dipole exerts a field which influences the orientation of its neighbors. The result will be either an increase or a decrease in the effective mean value of μ^2 , depending on the manner in which the dipoles associate. This effect will be expected to exist also in the pure liquid; it is not predicted by Onsager's theory because in that theory a polarizable continuum is used as a model for the environment of the polar molecule. Kirkwood (16) has recently devised a very elegant theoretical treatment which takes the effect of association formally into account and places the theory of liquid dielectrics on a firmer foundation. For a liquid made up of molecules of dipole moment μ and polarizability zero (i.e., $n^2 = 1$), Kirkwood has derived an equation of the same form as equation 9, but with n^2 replaced by unity and μ^2 replaced by $\mathbf{\mu} \cdot \bar{\mathbf{\mu}}$. The quantity $\bar{\mathbf{\mu}}$ is the average resultant of the moments of all molecules included within a spherical volume, of radius large compared with molecular dimensions, circumscribed about a given dipole as center, and the dot product $\mathbf{\mu} \cdot \bar{\mathbf{\mu}}$ is a vector notation for $\mu \bar{\mu} \cos \theta$, where θ is the angle between $\mathbf{\mu}$ and $\bar{\mathbf{\mu}}$. Since Kirkwood's equation was derived by a rigorous application of the methods of classical statistics and does not depend for its validity on a geometrical model, it will be expected that Onsager's equation should contain a quantity analogous to $\mathbf{\mu} \cdot \bar{\mathbf{\mu}}$ in place of μ^2 .

The dipole association referred to here is not to be confused with chemical association; its effect on the thermodynamic properties of the liquid will be much smaller and more subtle than the effect of chemical association. The aggregates of molecules mentioned above are not to be considered as chemical polymers but rather as aggregates of the type which, because of the attraction between positive and negative ions, occurs in solutions of strong electrolytes. If chemical association does occur, as it does for instance in hydrogen-bonding liquids, it may be expected of course to have a pronounced effect on the average value of μ^2 .

The effect of association is formally accounted for in Kirkwood's equation by the quantity $\mathbf{\mu} \cdot \bar{\mathbf{\mu}}$, which is to be calculated by statistical methods; the calculation of this quantity is unfortunately extremely difficult. If the dipole axis is also an axis of symmetry of the molecule, however, and only dipole-dipole interactions are involved, it can at least be predicted that $\bar{\mathbf{\mu}}$ will be parallel to $\mathbf{\mu}$. In the present paper an attempt will be made to predict, from a consideration of the structure of the molecules which make up the liquid, whether $\mathbf{\mu} \cdot \bar{\mathbf{\mu}}$ will be greater or less than μ^2 .

We shall divide dipole association into two classes: *co-association*, in which the dipoles prefer to orient head to tail, so that their moments reinforce one another, and *contra-association*, in which the dipoles tend to orient in an antiparallel configuration, so that their moments cancel.

Co-association will increase the value of $\mathbf{u} \cdot \bar{\mathbf{u}}$ relative to μ^2 ; contra-association will decrease it. It will be recalled that the potential energy of one dipole in the field of another is

$$V = \frac{\mu_1 \mu_2}{r^3} \{ \cos(\mu_1, \mu_2) - 3 \cos(\mu_1, r) \cos(\mu_2, r) \}$$

where (μ_1, r) is the angle between the dipole μ_1 and the radius vector r from μ_1 to μ_2 . On the basis of this formula and the structure of the molecule, we make the qualitative prediction that in liquid diethyl ether co-association will predominate, because configurations such as that shown in figure 1a are energetically much more favorable than those which contribute to contra-association. We shall therefore expect values of μ^2 calculated from the dielectric constant of diethyl ether by means of equation 9 or 12 to be too large. In liquid chlorobenzene, on the other hand, since configurations such as that shown in figure 1b are energetically favorable, contra-association will be expected to predominate; values of

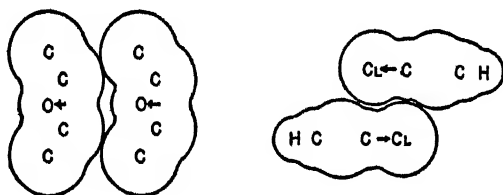


FIG. 1. (a) Co-association of ether molecules; (b) contra-association of chlorobenzene molecules.

the dipole moment of chlorobenzene calculated by means of equation 9 or 12 will be too low. The association error will be expected to decrease as the temperature increases or as the concentration of polar solute in a non-polar solvent approaches zero. It will be found later that the results of the application of Onsager's theory to the dielectric constants of polar liquids can be interpreted consistently on the basis of a consideration of the association error alone. The possibility is thereby suggested that in polar liquids the association error is considerably more important than is the reaction field error in causing Onsager's equation to deviate from agreement with experiment. Before considering the experimental applications in detail, it may be well to review briefly some critical discussions of Onsager's theory which have been carried out by Van Vleck and his associates.

Van Vleck (38, 39) has shown that the Onsager internal field is more consistent with a statistical-mechanical treatment of dipole-dipole coupling

than is the Clausius-Mossotti field, and has shown that Onsager's theory will explain the fact that the marked dielectric saturation predicted by the Clausius-Mossotti theory for polar liquids in moderately strong fields does not occur. Van Vleck also mentions a possibility suggested by H. Mueller (39), namely, that since the period of free rotation of a molecule is much smaller than the relaxation time of a polar dielectric, the liquid surrounding a dipole may not have time to adjust its polarization to the changing field of the rotating dipole. This effect, if it existed, would result in a value of the reaction field much smaller than that calculated by Onsager. It is difficult to decide *a priori* how much weight should be given to Mueller's suggestion. It may be mentioned, however, that Kirkwood (15) has shown that in a gas at ordinary temperatures a dipole molecule has the same effective mean square moment whether interacting with the field of another freely rotating dipole or with an external electric field. It is, moreover, in better accord with modern ideas of the structure of liquids to consider a molecule in a liquid not as freely rotating but rather as oscillating about a changing position of equilibrium whose rate of change is slow compared with the rate of free rotation. In view of these considerations it should be possible for the reaction field to follow the changing position of the dipole fairly closely. It will be shown later that there are empirical reasons for believing that the effect suggested by Mueller is not important.

Mention should be made of the information which can be gained from the dielectric constants of polar liquids by the application of Kirkwood's theory (16) in the form which takes into account the polarizability of the molecules in the liquid. By means of this theory an accurate value of the quantity $\mu_L \cdot \bar{\mu}_L$ can be calculated from the dielectric constant of a polar liquid. The quantity μ_L is the dipole moment of a molecule in the liquid, and differs from the gas value μ_g by the extra polarization due to the reaction field; $\bar{\mu}_L$ is related to μ_L in the manner previously described, and is a measure of dipole association in the liquid. In calculating the quantity $\mu_L \cdot \bar{\mu}_L$ from the dielectric constant by means of Kirkwood's theory, one gains an accurate knowledge of the combined effects of the reaction field and of what we have called the association effect, but no knowledge of the effect of either one alone. This fact is not surprising, since the two effects are manifestations of intermolecular interaction and are interdependent. In the present discussion of the application of Onsager's theory we are really making an artificial separation of the effect of intermolecular interaction into two parts: the reaction field effect which results in an increase of the average moment of the polar molecules in the liquid, and the association effect which is a measure of the extent to which the orientation of a given dipole in the applied field is influenced on the average by the action of its neighbors.

APPLICATIONS OF ONSAGER'S THEORY TO POLAR LIQUIDS

The relation of Onsager's equation 9 to the empirical equations mentioned previously will first be discussed. Onsager showed (24) that for large values of the dielectric constant equation 9 approximates the empirical equation of Wyman (43). It has furthermore been shown by Böttcher (1) that equation 9 can be put in the form of the semi-empirical equation 2 of van Arkel and Snoek, and that the empirical constant C of the latter equation is then identified with the expression

$$\frac{4\pi}{3} \frac{2\epsilon - 2}{2\epsilon + 1} \frac{n^2 + 2}{3}$$

In table 1 values of $\frac{3}{4\pi} C$ for pure ethyl bromide, as calculated from the above expression, are compared with the experimental values calculated by Smyth (30). The values of ϵ have been taken from Smyth and

TABLE 1
Comparison of values of $\frac{3}{4\pi} C$ for ethyl bromide

| $t, ^\circ\text{C} \dots\dots\dots$ | -90 | -50 | -10 | +30 |
|--|------|------|------|------|
| $\frac{3}{4\pi} C$ (experimental)..... | 1.49 | 1.43 | 1.38 | 1.32 |
| $\frac{3}{4\pi} C$ (theoretical)..... | 1.36 | 1.30 | 1.24 | 1.18 |

Morgan (27) and the values of n^2 have been calculated from the value of $P_E + P_A = 21.5$ cc. (29).

The theoretical and experimental values show fair agreement in magnitude and change in a similar way with increasing temperature.

An extensive comparison of equation 9 with experimental data on pure polar liquids has been undertaken by Böttcher (2) in a paper which contains a very complete compilation of dielectric constants and densities of polar liquids at various temperatures. The procedure was to compute values of n^2 using the electronic polarizability P_E alone; the latter quantity was obtained by extrapolating the mole refractivity to infinite wave length. Values of μ were then calculated from equation 9. The dipole moments calculated in this way depend to only a slight extent on the temperature and agree fairly well with those calculated from dielectric constant measurements on gases; in many cases they agree better with the gas values than do those obtained by the application of equation 1 to the dielectric con-

stants of dilute solutions of polar substances in non-polar solvents. Some of the results of Böttcher's computations are shown in table 2.

The excellence of this agreement is empirically useful but theoretically surprising and in the opinion of the present author is probably due to a fortuitous cancellation of errors. In view of the association error, the reaction field error, and the error involved in the neglect of optical anisotropy, equation 9 would hardly be expected to lead to correct values of the dipole moment; the results obtained by Böttcher indicate that approximate compensation for these errors can be made by using a value of n^2 smaller than the correct one.

TABLE 2
Böttcher's dipole moment values
Calculated from dielectric constants of liquids

| LIQUID | μ CALCULATED | μ GAS VALUE | μ SOLUTION VALUE |
|-----------------------------|---------------------|--------------------|-------------------------|
| Nitrobenzene..... | 4.2 | 4.2 | 3.9-4.1 |
| Nitromethane..... | 3.7 | 3.4 | 3.0-3.1 |
| <i>o</i> -Nitrotoluene..... | 3.9 | 3.6 | 3.7 |
| Acetone..... | 3.0-3.1 | 2.8 | 2.7-2.8 |
| Aniline..... | 1.5 | 1.5 | 1.5-1.6 |
| Acetonitrile..... | 3.6 | 3.9 | 3.1-3.5 |
| Benzonitrile..... | 3.6-3.7 | 4.4 | 3.9 |
| Anisole..... | 1.5 | 1.2 | 1.2-1.3 |
| Methyl chloride..... | 1.8 | 1.8 | 1.6-1.8 |
| Methyl bromide..... | 1.6 | 1.8 | 1.5 |
| Methyl iodide..... | 1.3-1.4 | 1.6 | 1.4 |
| Ethyl bromide..... | 1.8-1.9 | 2.0 | 1.8-1.9 |
| Bromobenzene..... | 1.5-1.6 | 1.7 | 1.5-1.6 |
| Acetic acid..... | 1.3-1.7 | 1.7 | |
| Water..... | 3.0-3.1 | 1.8 | 1.7-2.0 |
| Ethyl alcohol..... | 2.8-3.1 | 1.7 | 1.7 |

The mole electronic polarizability P_E , and the molecular electronic polarizability α_E connected with it, may be defined for the low-frequency radiation used in measuring dielectric constants by the equation

$$P_E \rho / M = \frac{4}{3} \pi N \alpha_E = \frac{n_\infty^2 - 1}{n_\infty^2 + 2} \quad (14)$$

where n_∞ is a quantity obtained by extrapolating the optical index of refraction to infinite wave length. In order to calculate the temperature-independent term $\frac{4}{3} \pi N \alpha$, experimentally obtained from the study of the dielectric constant of a polar gas over a range of temperatures, however, it is found that a correction must be added to P_E . This correction is

called the atomic polarizability, P_A , and may be defined by the following equation in conjunction with equation 14:

$$(P_E + P_A) \rho / M = \frac{4}{3} \pi N \alpha \text{ (experimental)} = \frac{n_{\text{eff.}}^2 - 1}{n_{\text{eff.}}^2 + 2} \quad (15)$$

Neither the effective index of refraction, $n_{\text{eff.}}$, nor the quantity n_{∞} is a true index of refraction, since the dielectric constant for radiation of any frequency is equal to the square of the index of refraction for that frequency (provided of course that the magnetic permeability is close to unity). The quantity $n_{\text{eff.}}$ is to be regarded as a derived quantity related to that

TABLE 3
Table of data

| LIQUID | ϵ AT 0°C. | REFERENCE | $P_E + P_A$ | REFERENCE | μG | REFERENCE |
|----------------------|--------------------|-----------|-------------|-----------|---------|-----------|
| Ethyl iodide..... | 8.38 | (19, 28) | 25.7 | (29) | 1.90 | (29) |
| Ethyl bromide..... | 10.23 | (19, 27) | 21.5 | (29) | 2.02 | (29) |
| Ethyl ether..... | 4.80 | (19) | 25.8 | (10) | 1.14 | (10) |
| Chloroform..... | 5.17 | (19, 27) | 23.0 | (10) | 1.15 | (10) |
| Chlorobenzene..... | 6.04 | (19, 27) | 33.2 | (10) | 1.69 | (12) |
| Benzonitrile..... | 27.6 | (19) | 31.6 | (12) | 4.39 | (12) |
| Nitrobenzene..... | 39.8 | (19) | 36.2 | (12) | 4.23 | (12) |
| Acetone..... | 21.58 | (19) | 18.4 | (10) | 2.84 | (46, 32) |
| Methyl chloride..... | 12.61* | (21) | 13.6 | (29) | 1.86 | (29) |
| Methyl bromide..... | 9.97 | (21) | 15.4 | (29) | 1.78 | (29, 14) |
| Methyl alcohol..... | 35.8 | (19) | 8.6 | (30) | 1.69 | (30) |
| Ethyl alcohol..... | 27.9 | (19) | 13.6 | (30) | 1.70 | (30) |
| Acetic acid..... | 6.17† | (19) | 12.9‡ | (44) | 1.73 | (44) |
| Water..... | 83.2 | (18) | 3.9 | (13) | 1.84 | (13) |

* At 20°C.

† At 20°C.

‡ Estimated from optical data.

part of the polarizability of a polar gas which does not depend on the orientation of permanent dipoles; it is this quantity which in our opinion should be used as the n of equation 9.

The physical significance of the atomic polarizability P_A has been discussed in detail by Van Vleck (37); the quantity is interpreted as being that part of the polarizability which arises from vibrations of the nuclei. In Böttcher's treatment it is implicitly assumed that P_A is negligible in liquids, whereas it is probable that in many liquids its value is slightly greater than in the gas.

There will now be presented the results of some calculations which were carried out in order to ascertain the extent to which dipole moments cal-

culated by means of equation 9 from the dielectric constants of polar liquids differ from the accepted values. The data which were used are shown in table 3.

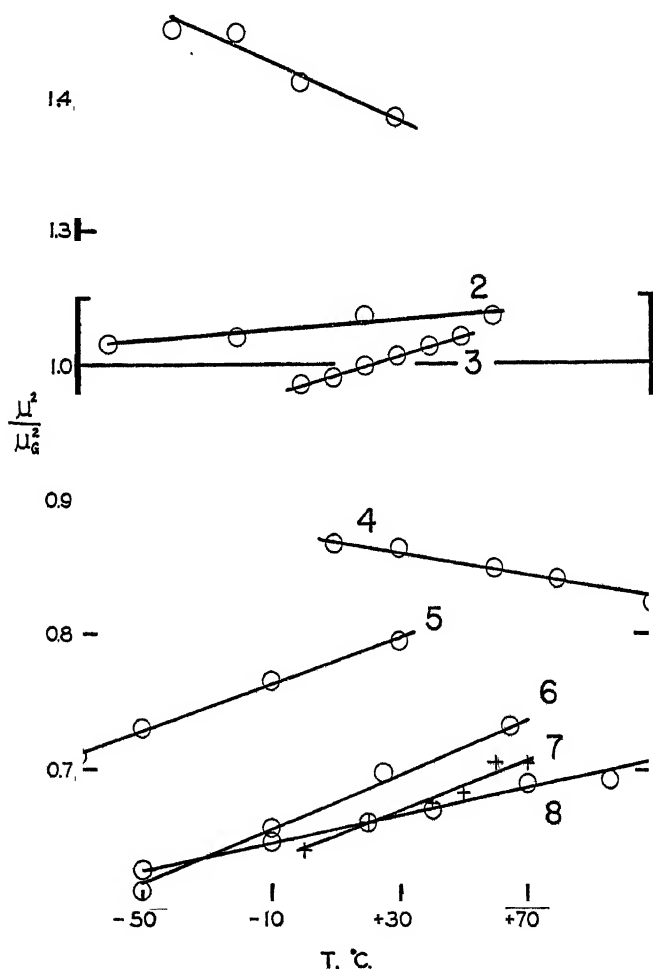


FIG. 2. Values of μ^2/μ_a^2 calculated by means of the unmodified Onsager equation (equation 9) from the dielectric constants of the following pure liquids: 1, diethyl ether; 2, chloroform; 3, acetone; 4, nitrobenzene; 5, ethyl bromide; 6, ethyl iodide; 7, benzonitrile; 8, chlorobenzene.

The values of $P_E + P_A$ and of μ_a , the permanent dipole moment of the free molecule, have been taken from the results of recent measurements of the dielectric constants of gases. The dielectric constant at 0°C. is

listed for each liquid, together with the reference from which the dielectric constant measurements were taken. At each temperature for which a calculation has been made, a value of n^2 was computed by means of equation 15 from the density of the liquid at that temperature and was used, together with the experimental dielectric constant, to calculate a value of μ^2 from equation 9. The results are shown in figure 2, in which the ratio of μ^2 to the accepted value μ_G^2 is plotted as a function of temperature.

A qualitative estimate of the association error to be expected can be made by a consideration of the molecular models shown in figure 3; these

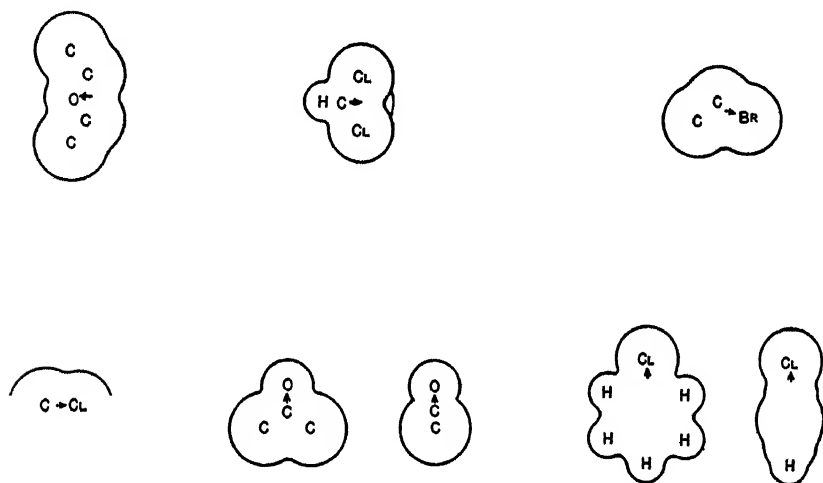


FIG. 3. Molecular models drawn to scale according to the bond distances and van der Waals' radii given by Pauling (25): A, diethyl ether; B, chloroform; C, ethyl bromide; D, methyl chloride; E, acetone; F, chlorobenzene. For each of the last two compounds two views are given: one from a direction perpendicular to the plane of the molecule, the other from a direction lying in the plane.

models have been drawn approximately to scale with the aid of the bond distances and van der Waals' radii given by Pauling (25). The estimated position of the effective dipole is indicated by a short heavy arrow.

It is evident that Onsager's molecular model is approximated more closely by the structures of chloroform and acetone than by the others. We shall therefore expect the dipole moment values calculated for these substances to show relatively close agreement with the accepted values. We shall, however, expect a small co-association error (too high a value of μ) for chloroform, and a small contra-association error (too low a value of μ) for acetone. Ether, on the other hand, should show a relatively large co-association error; the halides should show contra-association errors

which increase in the order methyl halide, ethyl halide, phenyl halide. The values of μ^2/μ_G^2 should moreover approach but not cross the value unity as the temperature increases. It is seen from the curves shown in figure 2 that the results obtained by the use of equation 9 are not altogether satisfactory.

A similar calculation in which the optical anisotropy was taken into account has been carried out by means of equation 12 with more satisfactory results. The calculation of n_1^2 was made by use of the equation

$$\frac{n_1^2 - 1}{n_1^2 + 2} M/\rho = (P_E + P_A)_1 \quad (16)$$

Assuming

$$(P_E + P_A)_1 = \frac{\alpha_1}{\alpha} (P_E + P_A) \quad (17)$$

where α_1 and α are, respectively, the molecular polarizability along the axis of the permanent dipole and the polarizability averaged over all directions. The value of α_1/α for ethyl bromide was estimated from data on the depolarization of light by the gas (33); for all other substances which were considered, values were taken from the table compiled by Stuart and Volkmann (34). All these values are for visible light. The assumption 17 is, of course, an approximation but should not cause serious error. The values of $(P_E + P_A)_1$ which were used are as follows: ethyl bromide, 27.5 cc.; acetone, 20.6 cc.; ethyl ether, 23.2 cc.; chloroform, 18.65 cc.; chlorobenzene, 43.2 cc.; nitrobenzene, 49.7 cc.

The results are shown in figure 4. The sign of the error in μ^2 appears in all cases to be consistent with the qualitative predictions which would be made on the basis of a knowledge of molecular structure, and in no case is there a trend of the ratio μ^2/μ_G^2 away from unity with increasing temperature. It is evident that much better qualitative agreement between Onsager's theory and the results of experiment is obtained if the optical anisotropy of the polar molecule is taken into account. The results may be considered as furnishing a rough measure of the magnitude of the association error, and as providing some information regarding the average environment of molecules in polar liquids.

The effects of association will be expected to be especially pronounced in hydrogen-bonding liquids such as water, alcohols, and organic acids. Values of the ratio μ^2/μ_G^2 have been calculated by means of equation 9 for several of these liquids and have been found to vary as follows: for water, from 2.76 at 12.5°C. to 2.54 at 100°C.; for methyl alcohol, almost constant at 3.0 from 0°C. to 60°C.; for ethyl alcohol, from 3.1 at 0°C. to 3.0 at 55°C.; for acetic acid, from 0.55 at 10°C. to 0.91 at 80°C. Equation 12 was not used in this calculation because the orientation of the polar-

izability ellipsoid is not known for any of these molecules except water. The results of the calculation indicate that for water and the alcohols $\bar{\mu}$ as defined by Kirkwood is several times larger than μ . No very detailed evidence regarding the nature of the association in the liquid is thereby obtained, since the angle between $\bar{\mu}$ and μ is not known. Moreover, the

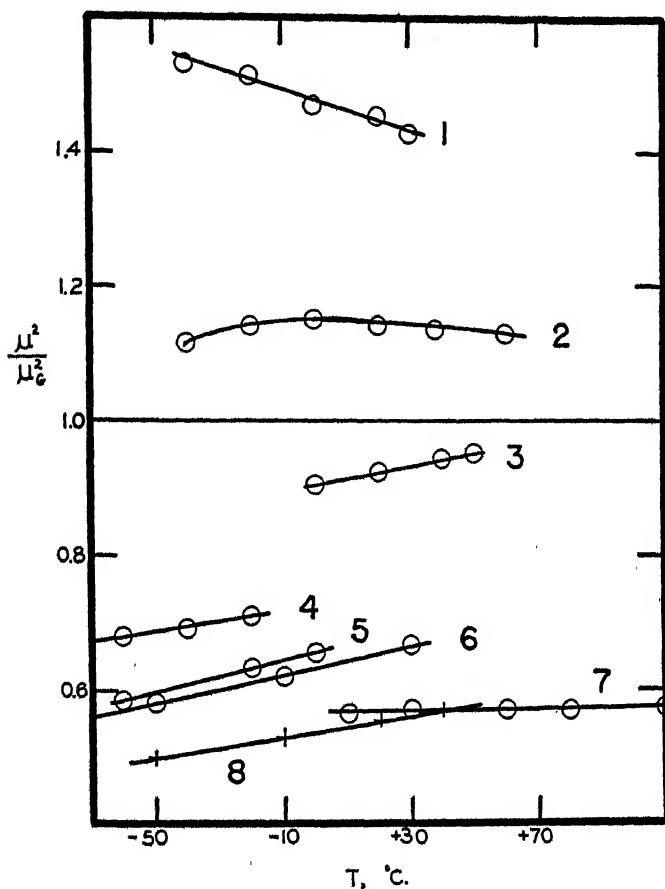


FIG. 4. Values of μ^2/μ_0^2 calculated by means of the modified Onsager equation from the dielectric constants of the following pure liquids: 1, diethyl ether; 2, chloroform; 3, acetone; 4, methyl chloride; 5, methyl bromide; 6, ethyl bromide; 7, nitrobenzene; 8, chlorobenzene.

associating molecules reinforce one another; in acetic acid, that form of application of equation 9 gives only approximate average values of the effective value of μ^2 , since the reaction field error in strongly associated liquids is probably large. It is clear, however, that in water and the alcohols association occurs largely in such a way that the moments of

association predominates in which the moments of associating molecules are opposed. These results are in accordance with Pauling's discussion (25) of hydrogen-bond formation in alcohols and organic acids, and with the experimental evidence compiled by him.

In the discussion of the criticisms which have been directed at Onsager's theory it was mentioned that Mueller (39) had suggested that the value of the reaction field calculated by Onsager might be too large, because of the inability of neighboring polar molecules to follow the motion of a given dipole. It is possible to carry out an empirical test of Mueller's suggestion by deriving an equation similar to equation 12 but using n^2 instead of ϵ in the expression for the reaction field. This is equivalent to assuming that the dipoles surrounding a given dipole are unable to follow the motion of the latter at all, and thus represents the most extreme possible application of Mueller's criticism. By means of the equation so derived, values of μ^2/μ_G^2 have been calculated and examined as before for consistency with the predicted effects of the association error. The values obtained in this way, over the same range of temperatures as given in figure 4, are about 0.75 for chlorobenzene, 0.9 to 1.0 for ethyl bromide, 1.1 to 1.0 for nitrobenzene, 1.3 for acetone, 1.45 to 1.39 for chloroform, and 1.9 to 1.8 for ether. These values do not appear reasonable in view of our previous considerations. We conclude that, empirically at least, the effects suggested by Mueller do not occur in an important way, though the possibility has not been eliminated that they may occur to a small extent.

APPLICATION OF ONSAGER'S THEORY TO POLAR SOLUTIONS

In his original paper Onsager (24) developed an extension of equation 9 to account for the dielectric constants of polar solutions. By means of the same procedure as he used, an equation may be derived which is an extension of equation 12 and takes into account the optical anisotropy of the polar molecule; for a solution of a single polar solute in a non-polar solvent this equation is

$$\frac{\epsilon - 1}{\epsilon} = \frac{4\pi N_2}{9kT} \frac{\mu_2^2 (n_{21}^2 + 2)^2 (2\epsilon + 1)}{(2\epsilon + n_{21}^2)^2} + \frac{3\theta_2 (n_2^2 - 1)}{(2\epsilon + n_2^2)} + \frac{3\theta_1 (n_1^2 - 1)}{2\epsilon + n_1^2} \quad (18)$$

Here ϵ is the dielectric constant of the solution, N_2 is the number of polar molecules per cubic centimeter of solution, and θ_2 , θ_1 are the fractions of the total volume occupied by polar solute and non-polar solvent, respectively. The average index of refraction n_2 of the polar molecule and the index of refraction n_{21} corresponding to polarization along the axis of the permanent dipole, are calculated as before from equations 15 and 16 with the use of values of M and ρ for the pure polar liquid at the temperature T . The value of n_1^2 , the square of the index of refraction of the solvent, has

been taken as equal to the dielectric constant of the solvent at the given temperature T . In the calculations whose results are presented here the following expressions have been assumed for N_2 , θ_2 , and θ_1 :

$$\begin{aligned} N_2 &= - \frac{N_A \rho}{M_2 + \frac{1-X}{X} M_1} \\ \theta_2 &= \left(1 + \frac{M_1 \rho_2}{M_2 \rho_1} \frac{1-X}{X} \right)^{-1} \\ \theta_1 &= \left(1 + \frac{M_2 \rho_1}{M_1 \rho_2} \frac{X}{1-X} \right)^{-1} \end{aligned} \quad (19)$$

where X is the mole-fraction of polar solute, ρ is the density of the solution; M_2 , M_1 are the molecular weights of solute and solvent, respectively; ρ_2 , ρ_1 are the densities of the corresponding pure liquids; and N_A is Avogadro's number.

No detailed derivation of equation 18 will be given here; the principal new assumption involved in its development is

$$\frac{4\pi}{3} (N_1 a_1^3 + N_2 a_2^3) = 1 = \theta_1 + \theta_2 \quad (20)$$

where a_1 and a_2 are the cavity radii for molecules of solvent and solute, respectively.

The measured dielectric constants and densities of polar solutions have been used to calculate values of μ^2 for the polar solute by means of equation 18. The results are expressed as before in the form of the ratio μ^2/μ_G^2 , which is plotted in figure 5 as a function of the concentration c of polar solute. In accordance with our expectations the curves for ethyl bromide and chlorobenzene are seen to approach the value unity as the concentration decreases. The behavior shown by the curve for chloroform is difficult to understand but may be due to small errors in the dielectric constant measurements, or to an error in the choice of the value of n^2 , or to a large reaction field error. The curve calculated from dielectric constants of very dilute solutions of acetone in benzene, and shown in figure 6, is quite satisfactory, however. The association error in this case is small, as would be expected. It is possible to extrapolate this curve to infinite dilution; the fact that the extrapolated value of μ^2/μ_G^2 (0.96) is not exactly equal to unity is not surprising, inasmuch as the reaction field error will be expected to exist even at infinite dilution.

Some years ago a calculation was made by Fuoss (11) which showed that in dilute polar solutions the effective value of μ^2 for a polar solute

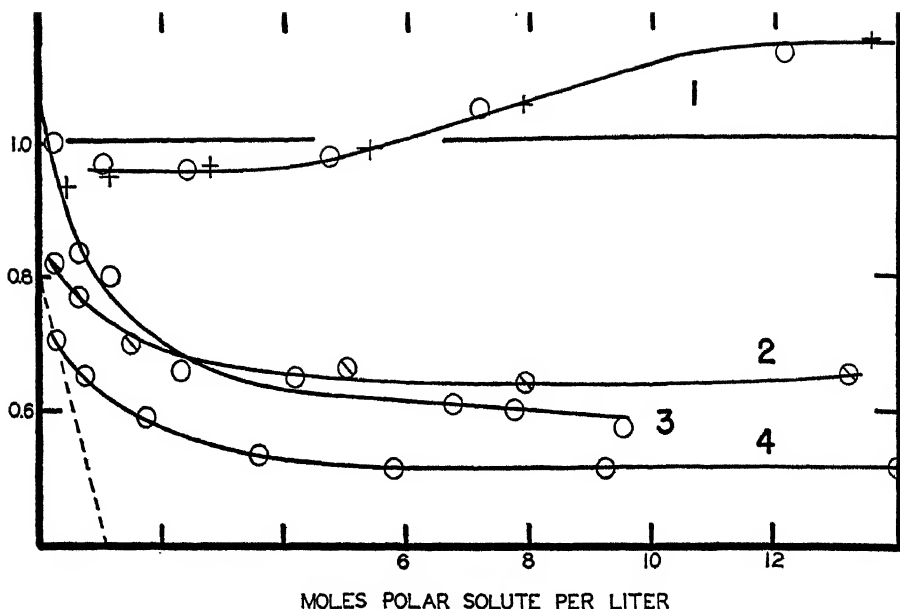


FIG. 5. Values of μ^2/μ_0^2 for the polar solute, calculated from the dielectric constants of hexane solutions of the following: 1, chloroform (circles refer to measurements at 40°C.; crosses to measurements at -50°C.); 2, ethyl bromide at 40°C.; 3, chlorobenzene at 50°C.; 4, ethyl bromide at -90°C. Experimental data in all cases were taken from Smyth and Morgan (27). The limiting slope calculated for ethyl bromide at 40°C. by means of the theory of Fuoss is shown by the dotted line.

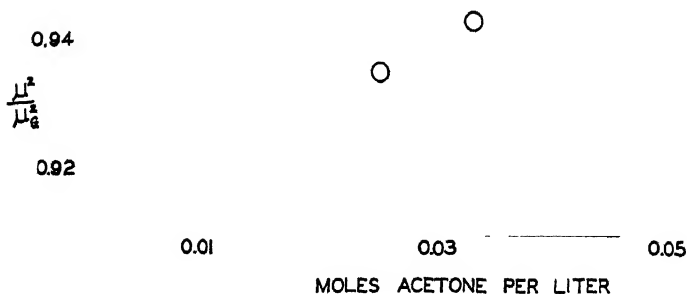


FIG. 6. Values of μ^2/μ_0^2 calculated from the dielectric constants of dilute solutions of acetone in benzene at 22°C. Measurements by Wolf and Gross (43).

would be expected to change rapidly with concentration because of the formation of dipole pairs which would not be oriented in the applied field

as would be a free dipole. Fuoss found that, because of this effect, the effective value of μ^2 in dilute polar solutions is

$$\mu_{\text{eff}}^2 = \mu_0^2 \left\{ 1 + \frac{N}{4\pi} \int \int \int e^{\frac{-u_m}{kT}} r^2 dr dw' dw'' \right\} \quad (21)$$

where μ_0 is the moment of a free dipole in the liquid, r is the distance between two interacting dipoles, dw' and dw'' are elements of solid angle which determine their relative orientation, and u_m is the interaction energy of two dipoles in the liquid, expressed as a function of r , w' , and w'' . The right-hand side of equation 21 is essentially equal to Kirkwood's quantity $\bar{\mu} \cdot \bar{\mu}$ for the special case of a solution sufficiently dilute that only interactions between pairs of dipoles need be considered. For an idealized molecular model, namely, an ellipsoid of revolution containing at its center a dipole of moment μ_0 oriented parallel to the major axis, it has been shown by Fuoss that the integral in equation 21 is approximately equal to

$$-4\pi \left(\frac{\pi}{3} \right)^{3/2} \frac{\mu_0^2}{\epsilon kT} \frac{Ze^y}{y^{7/2}} \quad (22)$$

where a is the major axis of the ellipsoid, b is the minor axis, $\lambda = b/a$,

$$= \left(\frac{1}{2\lambda^2} - 1 \right)^{-1/2} \quad y = \frac{\mu_0^2}{b^3 \epsilon kT}$$

and ϵ is the dielectric constant of the solution. Reference to figure 3 shows that the structure of ethyl bromide corresponds roughly to Fuoss' model; the expression 22 has accordingly been computed for a dilute solution of ethyl bromide in hexane at 40°C., and used to calculate

$$\frac{\partial}{\partial c} \left(\frac{\mu^2}{\mu_G^2} \right)_{c \rightarrow 0}$$

where c is the concentration of ethyl bromide in moles per liter. In this calculation the axes of the ellipsoid were assigned the values 7.0 and 4.3 Å.; the dipole moment μ_0 in expression 22 was corrected for the extra polarization produced by the reaction field, and ϵ was given the value 1.88, the dielectric constant of hexane at 40°C. The calculated value of the limiting slope was -0.36 ; a straight line of this slope is drawn in figure 5. The calculated slope is evidently of a reasonable order of magnitude, since it is possible that the curve for ethyl bromide should be extrapolated to a value of μ^2/μ_G^2 somewhat lower than unity because of the persistence of the reaction field error at infinite dilution. Too much significance should not be attached to the value -0.36 calculated for the slope, since there is considerable uncertainty regarding the appropriate choice of values of ϵ

and μ_0 to be applied in expression 22, and the structure of ethyl bromide is only a rough approximation to Fuoss' model.

In figure 7 is shown a curve in which values of μ^2/μ_G^2 for ethanol in benzene at 20°C. are plotted against the concentration of ethanol. In making this calculation n_{21}^2 was put equal to n_2^2 , since the orientation of the polarizability ellipsoid in ethanol is not known. The curve can be interpreted in the following way: In a concentrated solution high-order polymers

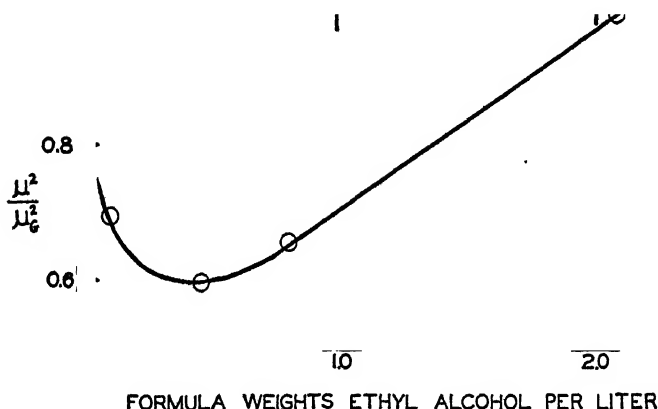
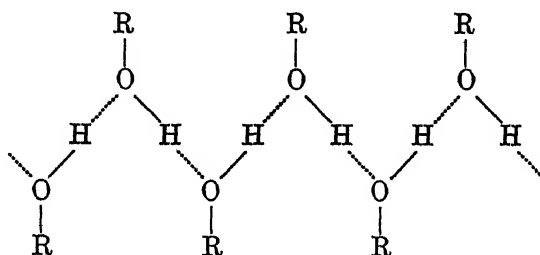


FIG. 7. Values of μ^2/μ_G^2 calculated for dilute solutions of ethanol in benzene at 20°C. Dielectric constant measurements by Smyth and Stoops (28).

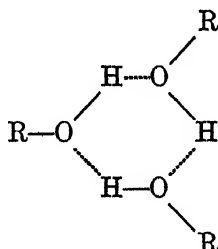
will be expected to predominate, many of which will have flexible chain structures of the following sort⁵ (25, pages 285-95):



These chains will have a large moment; their presence will cause a large increase in the mean value of μ^2 . The chains will have some tendency to form rings, however, since on ring closure the polymer is stabilized by the formation of an extra hydrogen bond; this tendency will be opposed by the decrease in entropy involved. In more dilute solutions polymers of lower order will predominate, and will have a greater tendency to form rings

⁵ The dotted lines indicate hydrogen bonds.

because the entropy decrease on ring closure is less for a short chain than for a long chain. The dipole moment of these rings will be small, as may be seen from the following possible structure for a trimer with zero moment:



The predominance of such ring structures may account for the minimum in the curve shown in figure 6. At still lower concentrations the monomer predominates, and the ratio μ^2/μ_a^2 approaches unity.

It is possible that in order to account for the ethanol curve it will be necessary to assume that the stable configuration of the dimer in dilute hexane solution is cyclic with zero moment. A further investigation of this possibility would be of interest, since there is at present no evidence for the existence of cyclic dimers of monobasic alcohols. At first glance a cyclic dimer, which would bring positively charged hydroxyl hydrogens close together and would make the R—O moments collinear and anti-parallel, would appear to be unstable relative to a chain dimer.

SUMMARY

A discussion has been given of Onsager's theory of liquid dielectrics and of its application to experiment. It has been shown that if Onsager's theory is modified to include the effect of optical anisotropy, the deviations of the modified theory from agreement with experiment can be consistently correlated with a qualitative discussion of the influence of molecular structure on intermolecular association in polar liquids. This result is somewhat surprising in view of the possibility that the value of the reaction field calculated by Onsager is for actual liquids seriously in error. It is difficult to believe that the observed consistency between the experimental data and the interpretation given here is the result of coincidence; this possibility must nevertheless be kept in mind. If, however, the interpretation given here is correct, the application of Onsager's theory to dielectric constant data can be used to obtain qualitative or perhaps even semi-quantitative information regarding the nature of intermolecular association in polar liquids and solutions; for example, the results given in the present paper indicate that in liquid diethyl ether, ethyl alcohol, and water the molecules are associated in such a way that the effective mean square

dipole moment is greater than that of a free molecule; in liquid aryl and alkyl monohalides, on the other hand, the effective mean square moment is less than that of a free molecule.

I am grateful to Professor J. G. Kirkwood for his kindness in making available to me, prior to publication, the results of his elegant theoretical treatment of the dielectric properties of polar liquids. I am also indebted to Dr. Lloyd Zumwalt, Dr. Saul Winstein, and especially to Professor Linus Pauling and Dr. Verner Schomaker for many helpful suggestions.

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APPENDIX A

Derivation of equations 3 and 4

It is known from the theory of electrostatics that the potential ψ in a region where there are no free charges must satisfy Laplace's equation $\nabla^2 = 0$. The field in any direction x is

$$E_x = -\frac{\partial\psi}{\partial x}$$

The following boundary conditions must also be satisfied: the potential must be a continuous function, and across any interface the normal component of the displacement vector $D = \epsilon E$ must be continuous. It is also required that the potential produced by the presence of polarizable bodies in the region must vanish at least as fast as $1/r$ at large distances. It can be shown that a solution of Laplace's equation which satisfies the conditions outlined above is a unique solution except for an additive constant.

Since we are interested in finding the field in a spherical cavity it will be convenient to use spherical polar coordinates r, θ, φ with origin at the center of the cavity. It is known that the general solution of Laplace's equation in these coordinates is a sum of spherical harmonics of the form

$$r^n P_n^m(\cos \theta)(A_{nm} \sin m\varphi + B_{nm} \cos m\varphi) \quad (1a)$$

and

$$r^{-(n+1)} P_n^m(\cos \theta)(A_{nm} \sin m\varphi + B_{nm} \cos m\varphi) \quad (2a)$$

where the A_{nm} and B_{nm} are constants, n is integral, and $P_n^m(\cos \theta)$ is an associated Legendre function of order m and degree n . In the cases we wish to consider it will be evident that the solutions must be cylindrically symmetric: i.e., with the proper choice for the orientation of the polar axis of the coordinate system, the solution of Laplace's equation will not depend on φ . Since this is the case, $m = 0$, and we need only consider the simple Legendre functions $P_n^0(\cos \theta)$ for the formation of possible solutions, e.g., $P_0^0(\cos \theta) = 1$; $P_1^0(\cos \theta) = \cos \theta$; $P_2^0(\cos \theta) = (3 \cos^2 \theta - 1)$; etc. In simple cases it can be decided by inspection which of these functions is likely to fit the boundary conditions.

Derivation of equation 4

We wish to discuss the modification of a homogeneous field E in an isotropic homogeneous medium of dielectric constant ϵ by the introduction of a cavity of radius a and dielectric constant unity. Let the unperturbed potential in the absence of the cavity be

$$\psi_0 = -Er \cos \theta$$

(i.e., the field E is directed along the polar axis). Let the potential after the introduction of the cavity be $\psi_0 + \psi_p$ outside the cavity, and ψ_i inside the cavity. The perturbation potential ψ_p must decrease at large distances from the cavity at least as fast as $1/r$. Each of these potentials must satisfy Laplace's equation, since outside the cavity

$$\nabla^2(\psi_0 + \psi_p) = 0 = \nabla^2\psi_0 + \nabla^2\psi_p = 0 + \nabla^2\psi_p$$

The boundary conditions are

$$(\psi_0 + \psi_p) = \psi_i \quad (r = a) \quad (3a)$$

$$\epsilon \frac{\partial}{\partial r} (\psi_0 + \psi_p) = \frac{\partial \psi_i}{\partial r} \quad (r = a) \quad (4a)$$

In view of these boundary conditions and the form of ψ_0 , an obvious solution to try is

$$\psi_i = -Br \cos \theta \quad (5a)$$

$$\psi_p = -\frac{A}{r^2} \cos \theta \quad (6a)$$

where A and B are undetermined constants. Substitute 5a, 6a, and the value of ψ_0 in equations 3a and 4a and solve with $r = a$. It is found that the boundary conditions are satisfied if

$$A = \frac{\epsilon - 1}{2\epsilon + 1} a^3 E$$

$$B = \frac{3\epsilon}{2\epsilon + 1} E$$

Then the field inside the cavity is

$$(3\epsilon/2\epsilon + 1)E = G \quad (\text{equation 4})$$

Derivation of equation 3

To find the field produced when a point-dipole of moment m is introduced at the center of a spherical cavity of radius a in a homogeneous isotropic medium of dielectric constant ϵ , in the absence of an applied field. Let the moment m be directed along the polar axis. Let the potential outside the cavity be ψ_e , and that inside the cavity be $\psi_0 + \psi_p$, where ψ_0 is the potential which would describe the field of the dipole in free space:

$$\psi_0 = \frac{m}{r^2} \cos \theta \quad (7a)$$

The boundary conditions are

$$\begin{aligned}\psi_0 + \psi_p &= \psi_e \quad (r = a) \\ \frac{\partial}{\partial r} (\psi_0 + \psi_p) &= \epsilon \frac{\partial \psi_e}{\partial r} \quad (r = a)\end{aligned}$$

In view of the form of ψ_0 , and of the fact that the potential of the dipole will be expected to fall off outside the cavity as $1/r^2$, we try the solution

$$\psi_p = Rr \cos \theta$$

$$\psi_e = \frac{C}{r^2} \cos \theta$$

The boundary conditions are satisfied by

$$\begin{aligned}R &= -\frac{2(\epsilon - 1)m}{2\epsilon + 1} \frac{1}{a^3} \\ C &= \frac{3m}{2\epsilon + 1}\end{aligned}$$

Within the cavity the field in the direction of the axis m , i.e., in the direction $\cos \theta = 1$, is

$$-\frac{\partial}{\partial r} (\psi_0 + \psi_p)_{\cos \theta = 1} = \frac{2m}{r^3} + \frac{2(\epsilon - 1)m}{2\epsilon + 1} \frac{1}{a^3}$$

The second term is the reaction field R , which will tend to increase the moment of the dipole in the cavity and acts parallel to the axis of the dipole. In vector notation its value is

$$R = \frac{2(\epsilon - 1)m}{2\epsilon + 1} \frac{1}{a^3} \quad (\text{equation 3})$$

APPENDIX B

Derivation of Onsager's equation

Solving equation 5 for m , one obtains

$$m = \mu u + \left(\frac{3\epsilon}{2\epsilon + 1} \alpha \right) E \left/ \left\{ 1 - \frac{2(\epsilon - 1)}{2\epsilon + 1} \frac{\alpha}{a^3} \right\} \right. \quad (1b)$$

Substitute

$$n^2 + 2 = \frac{2\epsilon}{a^3}$$

from equations 7 and 8, and simplify. The equation becomes

$$= \frac{(n^2 + 2)(2\epsilon + 1)}{3(2\epsilon + n^2)} \mu u + \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2} \alpha E \quad (2b)$$

$$= \mu' u + \beta E \quad (3b)$$

The torque acting on the dipole is $(\mathbf{R} + \mathbf{G})\mathbf{xm} = \mathbf{T}$. Since \mathbf{R} is parallel to \mathbf{m} , $\mathbf{R}\mathbf{xm} = 0$, and

$$\mathbf{T} = \mathbf{G}\mathbf{xm} = \frac{3\epsilon}{2\epsilon + 1} \mathbf{Ex}(\mu'u + \beta\mathbf{E}) = \frac{3\epsilon}{2\epsilon + 1} \mu' \mathbf{Exu} = \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2} \mu E \sin \theta = \mu^* E \sin \theta$$

where θ is the angle between \mathbf{E} and \mathbf{u} . The potential energy is then equal to

$$U = -\mu^* E \cos \theta \quad (4b)$$

The component of \mathbf{m} in the direction of \mathbf{E} is

$$m_E = \mu' \cos \theta + \beta E$$

In order to determine \bar{m}_E , the average value of m_E , it is necessary to find the average value of $\cos \theta$.

Using Boltzmann statistics, we obtain

$$\overline{\cos \theta} = \frac{\int_0^{2\pi} \int_0^\pi e^{-\frac{U}{kT}} \cos \theta \sin \theta \, d\theta \, d\varphi}{\int_0^{2\pi} \int_0^\pi e^{-\frac{U}{kT}} \sin \theta \, d\theta \, d\varphi}$$

For fields sufficiently small that powers of $\mu^* E/kT$ higher than the first are negligible, the above expression becomes

$$\overline{\cos \theta} = \frac{\mu^* E}{3kT}$$

Whence

$$\bar{m}_E = \frac{\mu' \mu^*}{3kT} E + \beta E = \left\{ \frac{(n^2 + 2)^2 (2\epsilon + 1)}{3(2\epsilon + n^2)^2} \frac{\mu^2}{3kT} + \frac{\epsilon(n^2 + 2)}{2\epsilon + n^2} \right\} \alpha E$$

To eliminate α and \bar{m}_E substitute

$$\alpha = \frac{3}{4\pi N} \frac{n^2 - 1}{n^2 + 2}$$

$$\bar{m}_E = \frac{\bar{P}}{N} = \frac{\epsilon - 1}{4\pi N} E$$

After simplification, equation 9 is obtained:

$$\frac{(\epsilon - n^2)(2\epsilon + n^2)}{\epsilon(n^2 + 2)^2} = \frac{4\pi N}{9kT} \mu^2$$

THE HYDROGEN PEROXIDE THEORY OF ELECTROLYTIC OXIDATION

S. GLASSTONE¹

Department of Chemistry, University of Sheffield, Sheffield, England

AND

A. HICKLING

Department of Chemistry, University College, Leicester, England

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I. INTRODUCTION

Electrolytic oxidation processes fall broadly into two classes involving reactions which are thermodynamically reversible and irreversible, respectively. In the first category,—as, for example, in the oxidation of ferrous to ferric ions, of ferrocyanide to ferricyanide, or of hydroquinone to quinone,—the process takes place at a definite potential almost identical with the reversible oxidation–reduction potential for the given system, and the electrode material, provided it is not attacked, has little influence, at least at low current densities. Apart from its effect on diffusion, which is only apparent at high currents, alteration of temperature does not produce any appreciable change either of the anode potential or of the efficiency of the oxidation reaction. When the electrolytic process is thermodynamically irreversible, however, as is the case in the oxidation of many organic compounds and of certain inorganic and organic anions, the phenomena are very complex and a satisfactory interpretation of the results appears difficult; it is this aspect of the subject of electrolytic oxidation with which the present review is concerned.

It had been assumed for many years that in electrolytic oxidation each definite electrode potential stage corresponded to a different process and that a high potential implied a more intense oxidation than a low one; an examination of the experimental data, however, shows that these views are incorrect. In the oxidation of thiosulfate to tetrathionate (18), of sulfite to dithionate (18), and of methyl alcohol (32, 42), formaldehyde (32, 42), formic acid (29, 31, 33), and ethyl alcohol (27) at platinum anodes, two distinct potential stages have been observed, but the nature

¹ Present address: Frick Chemical Laboratory, Princeton University, Princeton, New Jersey.

of the products appears to be the same at each stage and to be quite independent of the potential. Further, acetic acid can be oxidized anodically either to ethane or to methyl alcohol; the latter presumably represents a higher state of oxidation, but it is obtained, nevertheless, at a lower potential than the former (20). It is remarkable, too, in connection with these reactions that the addition of small amounts of neutral salts to acetic acid solution can cause almost complete suppression of the formation of ethane and its replacement by methyl alcohol (20). Another aspect of the difficulties involved in an interpretation of irreversible anodic phenomena is apparent when the influence of electrode material is considered. In the oxidation of acetate (20) and acid-ester ions (26) the efficiency is high for a smooth platinum anode but is low for an electrode of platinized platinum or lead dioxide; in the conversion of iodate to periodate (30) and of chromic to chromate ions (23), however, there is a complete reversal of this behavior. The effect of changes of temperature and of acidity or alkalinity seems, at first sight, to be equally paradoxical. Increase of pH, for example, results in a decrease of efficiency for the conversion of thiosulfate to tetrathionate (18), but alkalinity favors the oxidation of iodate (30) and chromic ions (23).

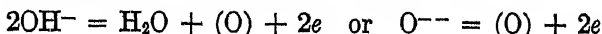
During recent years the authors of this paper have studied a number of electrolytic oxidation reactions, and, as a result, a theory has been developed providing an adequate explanation of the facts recorded above and many others brought to light in the course of the investigation. It is proposed to give here an account of the development of this theory and its application to the phenomena of electrolytic oxidation.

II. ORIGIN OF THE HYDROGEN PEROXIDE THEORY

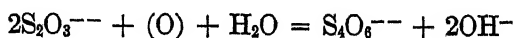
The anodic oxidation of sodium thiosulfate to tetrathionate can be formulated either as a purely electrical process,



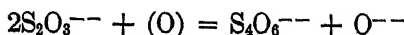
or as a chemical reaction brought about by active oxygen liberated at the anode by the discharge of hydroxyl or oxygen ions, thus:



followed by



or



Thatcher (43) considered the oxidation reaction to be chemical in nature; this conclusion rested mainly on the inference, based on observations of

electrode potential, that mercuric cyanide, which is a catalytic poison, inhibited the conversion of thiosulfate to tetrathionate. If the process were electrical in nature, it is improbable that a very small amount of mercuric cyanide would have any influence on the results, but if it involved a chemical reaction, with the electrode material acting as catalyst, traces of an active poison might be expected to inhibit the anodic oxidation.

In 1931 the present authors set out to test the value of, and if possible to utilize, Thatcher's observation as a criterion for distinguishing between chemical and electrical processes at an anode, and an examination was made of the electrolytic oxidation of sodium thiosulfate solutions. The experimental technique, involving the use of buffer solutions for the maintenance of constant pH, of electrodes with controlled oxygen content, and of an accurate analytical method for the estimation of tetrathionate, represented a marked advance on previous work; the results obtained were

TABLE 1

Influence of poisons and of copper ions on the electrolytic oxidation of sodium thiosulfate

| ADDED SUBSTANCE | CURRENT EFFICIENCY FOR OXIDATION |
|--|-------------------------------------|
| | <i>per cent</i> |
| None..... | 90 |
| 0.001 <i>M</i> mercuric cyanide..... | 91 |
| 0.01 <i>M</i> carbon disulfide..... | 91 |
| 0.01 <i>M</i> arsenious oxide..... | 87 |
| 0.005 <i>M</i> strychnine hydrochloride..... | 56 |
| 0.001 <i>M</i> copper sulfate..... | 30 |

thus reliable and easily reproducible. It was found that traces of mercuric cyanide in solution resulted in a definite increase of anode potential, as observed by Thatcher, but the efficiency of oxidation of thiosulfate to tetrathionate was almost unchanged. It is evident, therefore, that although the poison changes the electrode potential, it has no influence on the actual anodic process. In extending this work, the effect of other catalytic poisons, such as carbon disulfide, arsenious oxide, and strychnine hydrochloride, was investigated, and the influence of cupric ions, which are known to accelerate catalytically a number of reactions involving thiosulfate, was also studied. The results obtained for 0.025 *M* thiosulfate, in a buffer solution at pH 7, with a smooth platinum anode at ordinary temperature are quoted in table 1 (18); the current density (*C.D.*) employed was about 0.0002 ampere per square centimeter.

The data recorded in table 1 show that whereas some catalytic poisons, e.g., mercuric cyanide and carbon disulfide, have no influence on the anodic

oxidation of thiosulfate, others, e.g., arsenious oxide and especially strychnine hydrochloride, diminish the efficiency. Further, the surprising effect is evident that the expected catalyst, copper sulfate, also inhibits the electrolytic oxidation and to a marked degree. In seeking for a property possessed in common by arsenious oxide, strychnine salts, and copper ions, it became apparent that they were all catalysts for the decomposition of hydrogen peroxide, copper salts being particularly active in this respect. To test whether this common property was merely fortuitous, or whether it was fundamentally connected with the results obtained in the electrolysis of thiosulfate solutions, experiments were made in which a number of substances known to be effective catalysts for hydrogen peroxide decomposi-

TABLE 2

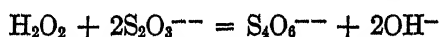
Influence of catalysts for the decomposition of hydrogen peroxide on the electrolytic oxidation of sodium thiosulfate

| Current density, in amperes per square centimeter | 0.0002 | 0.001 |
|---|----------------------------------|----------|
| CATALYST ADDED | CURRENT EFFICIENCY FOR OXIDATION | |
| | per cent | per cent |
| None..... | 90 | 85 |
| Animal charcoal, 0.5 g. per 100 ml..... | | 83 |
| Sheep's blood, 1 ml. per 100 ml..... | 85 | |
| Powdered silver, 0.5 g. per 100 ml..... | | 69 |
| Solid cobaltic oxide, 0.5 g. per 100 ml..... | | 59 |
| Cobalt sulfate, 0.001 <i>M</i> | | 31 |
| Ferrous sulfate, 0.001 <i>M</i> | 32 | |
| Copper sulfate, 0.001 <i>M</i> | 30 | |
| Solid manganese dioxide, 0.25 g. per 100 ml..... | 24 | |
| Manganous sulfate, 0.0001 <i>M</i> | | 3 |
| Manganous sulfate, 0.001 <i>M</i> | | 0 |

tion were added to the electrolyte. The catalysts chosen were as varied as possible in their chemical nature and were such as to be unlikely to react with either thiosulfate or tetrathionate ions. The data recorded in table 2 are for a 0.025 *M* solution of thiosulfate at pH 7, with a smooth platinum anode at ordinary temperature. These very remarkable results, and especially the fact that the presence of 0.001 *M* manganous sulfate is able to inhibit completely the electrolytic oxidation of thiosulfate ions, indicate clearly that hydrogen peroxide must play an important part in the reaction. The provisional assumption was made, therefore, that hydrogen peroxide is, at least in this instance, the effective anodic oxidizing agent, and further experiments were devised to test this view.

It has been known for many years (2) that the action of hydrogen

peroxide on sodium thiosulfate leads to two alternative processes resulting in the formation of tetrathionate and sulfate, respectively, thus:



and



The first reaction predominates in acid solution and is catalyzed by hydrogen ions, whereas the second tends to occur in neutral and alkaline media.

TABLE 3

Influence of hydrogen-ion concentration on the electrolytic oxidation of sodium thiosulfate

| pH | CURRENT EFFICIENCY | |
|----|--------------------|----------|
| | Tetrathionate | Sulfate* |
| | per cent | per cent |
| 5 | 90 | 5 |
| 6 | 87 | 9 |
| 7 | 79 | 11 |
| 8 | 65 | 12 |
| 9 | 60 | 14 |

* The figures for sulfate formation, while only approximate, are probably not seriously in error.

TABLE 4

Influence of molybdate ions on the electrolytic oxidation of 0.025 M sodium thiosulfate in the presence of 0.001 M manganous sulfate at pH 5

| | CURRENT EFFICIENCY | |
|-------------------------------------|--------------------|----------|
| | Tetrathionate | Sulfate |
| | per cent | per cent |
| Without molybdate..... | 94 | 1 |
| With 0.01 M ammonium molybdate..... | 61 | 34 |

It has been found that, in addition to tetrathionate, a small proportion of sulfate is formed in the course of electrolytic oxidation of thiosulfate; if hydrogen peroxide is the active oxidant, then the amount should increase as the solution becomes more alkaline. The experimental results in table 3, for a 0.025 M thiosulfate solution and a current density of 0.0002 ampere per square centimeter, show that this is in fact the case.

In feebly acid solutions molybdate ions markedly catalyze the formation of sulfate in the oxidation of thiosulfate ions by hydrogen peroxide; it was, therefore, of interest to see if a similar catalytic influence could be

observed in the electrolytic process. An examination of the results of Abel and Baum (1) suggested that the experimental conditions should be such that the concentration of hydrogen peroxide was low, consequently the electrolyte, which consisted of 0.025 *M* thiosulfate in a buffer solution at pH 5, was made 0.001 *M* with respect to manganous sulfate. Observations were made on two solutions, with and without ammonium molybdate, respectively, and sufficient electricity was passed to ensure almost complete oxidation of the thiosulfate in each case. The current density was 0.001 ampere per square centimeter, and the current efficiencies for the formation of tetrathionate and sulfate are given in table 4. The fact that the electrolytic oxidation of thiosulfate, like the oxidation by hydrogen peroxide, may be diverted to a large extent into an alternative path by the presence of molybdate ions, provides strong support for the view that hydrogen peroxide is the effective anodic oxidizing agent.

III. STATEMENT AND APPLICATION OF THE THEORY

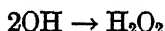
In view of the success of the hydrogen peroxide theory in accounting for the observations made in the electrolytic oxidation of thiosulfate, a comprehensive survey has been made of a number of other anodic reactions to see if a general theory of electrolytic oxidation could be developed. The behavior of sulfites (19), halides (21), chromic salts (23), acetates (20), and ester-acid salts, e.g., potassium ethyl malonate (26), has been investigated, and the theory of the anodic formation of hydrogen peroxide has assumed a form capable of interpreting experimental results of a very varied character.

A. The theory of the anodic formation of hydrogen peroxide

The primary postulate of the theory is that the OH radicals produced at the anode by the discharge of hydroxyl ions, which are always present in aqueous solutions, immediately combine *irreversibly* to form hydrogen peroxide, thus:



followed by the combination of the radicals in pairs,



If it is assumed that the *discharge* of hydroxyl ions occurs reversibly, then the requisite anodic potential will be given by an equation of the form

$$\pi = \pi_0 + \frac{RT}{F} \ln \frac{a_{\text{OH}}}{a_{\text{OH}^-}}$$

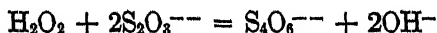
where a_{OH} and a_{OH^-} represent the activities of hydroxyl radicals and ions, respectively. If, as postulated, the radicals immediately combine *irre-*

versibly to give hydrogen peroxide, the term a_{OH} will be minute, and consequently the discharge potential of hydroxyl ions will be very low; hence this process will take precedence over, or will accompany to some extent, nearly all other anodic reactions. Under most conditions, therefore, it is to be expected that hydrogen peroxide will be formed, even at relatively low anode potentials, probably as a thin concentrated layer over the electrode surface. In the absence of a depolarizer capable of being oxidized, the hydrogen peroxide will decompose to give oxygen and water, but if a suitable depolarizer is present, it will bring about oxidation in its own characteristic manner; this may be accompanied by oxidation due to the nascent oxygen arising from the decomposition of the peroxide and possibly by evolution of oxygen gas. The extent to which oxidation by hydrogen peroxide takes place will depend on the stability of the latter under the conditions of electrolysis, and all factors capable of affecting the decomposition of the peroxide may be expected to have some influence on the electrolytic oxidation. The interpretation of anode potentials in relation to the theory of the anodic formation of hydrogen peroxide, and an explanation of the somewhat unexpected phenomena to which reference has been made in the introduction, will be discussed later (see section J).

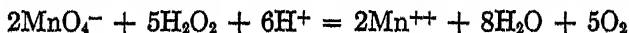
B. Nature of anodic products

The hydrogen peroxide formed at the anode in the manner suggested above can react in at least five ways:

(a) It may bring about oxidation by accepting electrons from the depolarizer and being reconverted into hydroxyl ions. An example of this type of behavior is the oxidation of thiosulfate already considered, thus:²



(b) The peroxide may bring about apparent reduction of highly oxidized compounds such as permanganate, chromate, and periodate ions, which react with hydrogen peroxide with the evolution of oxygen, e.g.,



(c) The reaction of non-ionized organic compounds with hydrogen peroxide may result in the introduction of hydroxyl groups into the molecule. An example of this type of behavior is the chemical reaction between the peroxide and benzene to give phenolic derivatives (see, e.g., 9, 27).

² It must not be assumed that writing the equation in this form implies any definite mechanism; it merely represents the net result of the process. It may be that S_2O_3^- ions are first formed and that these combine to give $\text{S}_4\text{O}_6^{--}$, or that an S_2O_3 radical is produced which reacts with an $\text{S}_2\text{O}_3^{--}$ ion.

(d) The hydrogen peroxide or the active oxygen arising from its decomposition may bring about oxidation of a general nature.

(e) If no suitable depolarizer is present, oxygen gas will be evolved as a result of the decomposition of the peroxide.

The anodic oxidation of thiosulfate, sulfite, acetate, and similar ions provides examples of reactions which are mainly of type (a); these processes will be considered briefly.

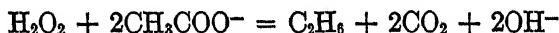
(1) Electrolytic oxidation of thiosulfate gives mainly tetrathionate, but as is to be expected this is accompanied by some sulfate, the amount depending on the experimental conditions as already described. Since thiosulfate is stable towards oxygen and does not take part in reactions of type (c), the only other alternative is evolution of oxygen gas according to reaction (e), and this occurs, although only to a small extent.

(2) Sulfite is oxidized anodically to dithionate, thus:

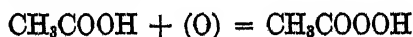


but it is always accompanied by a large proportion of sulfate. This may arise either from an alternative reaction with hydrogen peroxide, or as a result of oxidation produced by the decomposition of the peroxide (reaction (d)). Another possibility, at high current densities or with low concentrations of sulfite, is oxygen evolution (reaction (e)).

(3) The anodic oxidation of acetate ions results in the formation of ethane, together with carbon dioxide, according to the reaction



Under certain conditions methyl alcohol is the chief product, and this is probably the result of the decomposition of peracetic acid formed by a reaction of type (d), as follows:



and

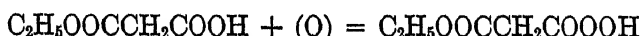


A small amount of gaseous oxygen is generally found among the anodic products.

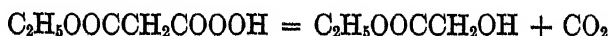
(4) Acid-ester salts, such as potassium ethyl malonate, undergo reactions similar to those described for acetate ions: with potassium ethyl malonate the chief product, in addition to carbon dioxide, is diethyl succinate. The oxidation may be written



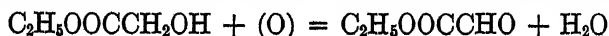
In addition to oxygen evolution (reaction (e)), some ethyl glyoxylate is formed, probably as a result of a primary reaction of type (d), thus:



followed by decomposition of the per-acid



and oxidation of the glycolate, probably by active oxygen, thus



The apparent reducing properties of hydrogen peroxide, referred to as reaction of type (b), account for the striking fact that in the electrolysis of acid solutions of permanganate and dichromate the proportion of oxygen evolved at the anode is appreciably greater than that required by Faraday's laws. The data recorded in table 5 give the ratio of oxygen to hydrogen

TABLE 5

Oxygen-hydrogen ratio in the electrolysis of acidified permanganate solutions

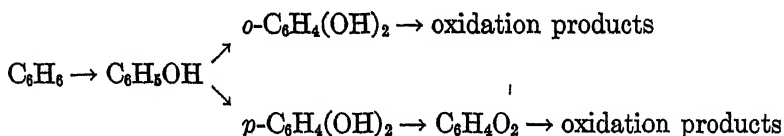
| CURRENT DENSITY | OXYGEN-HYDROGEN RATIO | |
|----------------------------|-----------------------------|---|
| | In 2 <i>N</i> sulfuric acid | In 2 <i>N</i> sulfuric acid plus <i>N</i> potassium permanganate |
| <i>amperes per sq. cm.</i> | | |
| 0.05 | 0.481 | 0.657 |
| 0.01 | 0.486 | 0.641 |
| 0.0036 | 0.492 | 0.543 |

obtained in the electrolysis of a 2 *N* sulfuric acid solution alone, and the same solution containing *N* potassium permanganate, at three different current densities; the time of electrolysis was 4 hr. in each case (24). The oxygen-hydrogen ratio in the sulfuric acid solution is seen to be slightly less than the theoretical value of 0.500; this is to be attributed to the formation of a small proportion of persulfuric acid. When perchloric acid was used as electrolyte, the ratio was 0.497 in the absence of permanganate, and 0.656 in its presence, at a current density of 0.05 ampere per square centimeter. With solutions containing dichromate the proportion of oxygen in the gases evolved on electrolysis is also higher than that obtained in an acid electrolyte alone, although the increase is not so great as in the permanganate solutions.

An interesting aspect of reaction (b) has been observed in connection with the electrolytic oxidation of chromic salts to chromate in acid solution; the actual oxidizing agent in this reaction is probably active oxygen

functioning through the formation of metallic peroxides with the electrode material. Since hydrogen peroxide formed anodically will tend by reaction (b) to convert the chromate back into chromic ions, however, the net efficiency of the oxidation is increased by the presence of catalysts able to bring about the decomposition of hydrogen peroxide (23).

In the electrolytic oxidation of aromatic hydrocarbons, e.g., benzene, toluene, and naphthalene, phenolic compounds are generally the primary products: in these cases reactions of type (c) are evidently of chief importance (10). Among the products of the oxidation of benzene, for example, there have been obtained phenol, catechol, quinol, and quinone; the processes may be represented thus:



The introduction of first one and then a second hydroxyl group may be attributed to the direct action of the hydrogen peroxide, but other products, such as quinone and maleic acid, are probably formed by active oxygen resulting from the decomposition of the peroxide (reaction (d)). The benzaldehyde and benzoic acid detected in the oxidation of toluene are no doubt also the result of a reaction of the latter type.

C. Influence of anode material

If hydrogen peroxide is produced anodically, as postulated, then the catalytic effect of the electrode material on the decomposition of the peroxide should be related in some manner to the oxidation efficiency. For reactions such as those of types (a) and (c), described above, the efficiency should be low if the anode is an active catalyst, but it should be high where processes of types (b) and (d) are involved. The experimental results are in general agreement with these anticipations.

The materials commonly employed as anodes fall broadly into three groups according to their effectiveness in catalyzing the decomposition of hydrogen peroxide. Smooth platinum, and gold and nickel free from higher oxides, are relatively poor catalysts; carbon is a moderate catalyst, although its activity depends upon the state of division of the surface; finally, platinized platinum, manganese dioxide, lead dioxide, and gold and nickel covered with their effective oxides,³ are good catalysts. In the

³ After electrolysis at high current densities, a nickel anode is usually found to be coated with a black deposit, probably nickel peroxide, and on being introduced into hydrogen peroxide solution causes vigorous momentary decomposition. The reaction is not truly catalytic, but is a mutual reduction and ceases when the nickel

presence of a good depolarizer, especially at low current densities, the surfaces of both gold and nickel remain free from higher oxides, and experiment has shown that the metals have then little catalytic activity, but at high current densities the metals, when used as anodes, become coated with dark colored oxides capable of bringing about vigorous decomposition of hydrogen peroxide.

It is now of interest to see how far the results obtained in various electrolytic oxidations may be correlated with the catalytic efficiencies of the

TABLE 6
Current efficiencies for oxidations with different anodic materials

| ANODE MATERIAL | REACTIONS† | | | | |
|----------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| | I | II | III | IV | V |
| | <i>per cent</i> | <i>per cent</i> | <i>per cent</i> | <i>per cent</i> | <i>per cent</i> |
| { Smooth platinum..... | 76 | 28 | 89 | 74 | 1 |
| { Gold..... | 65 | 28 | | | |
| { Nickel..... | 60 | 32 | | | |
| Carbon*..... | 51 | 3 | 21 | 22 | 1 |
| { Platinized platinum..... | (91) | 7 | 3 | 0 | 53 |
| { Manganese dioxide..... | 0 | 2 | 0 | | 19 |
| { Lead dioxide..... | | | 0 | 0 | 100 |
| { Gold covered with oxide..... | | | 0 | 12 | |
| { Nickel covered with oxide..... | | | 0 | | |

* Various forms of carbon give different results; those quoted are for gas carbon.

† The reactions are: I $\text{S}_2\text{O}_8^{--} \rightarrow \text{S}_4\text{O}_8^{--}$

II $\text{SO}_3^{--} \rightarrow \text{S}_2\text{O}_6^{--}$

III $\text{CH}_3\text{COO}^- \rightarrow \text{C}_2\text{H}_6 + 2\text{CO}_2$

IV $\text{C}_2\text{H}_5\text{OOCCH}_2\text{COO}^- \rightarrow \text{C}_2\text{H}_5\text{OOCCH}_2\text{CH}_2\text{COOC}_2\text{H}_5 + 2\text{CO}_2$

V $\text{Cr}^{+++} \rightarrow \text{CrO}_4^{--}$

materials used as anodes, and some relevant facts have been collected in table 6. Apart from the exceptional behavior of platinized platinum in the oxidation of thiosulfate, which is undoubtedly to be attributed to the poisoning action of the latter (7, 18), it is quite clear that in reactions I, II, III, or IV, which are all of type (a), involving direct action between hydrogen peroxide and the depolarizer, the highest efficiencies are obtained

peroxide is reduced. Since, however, the oxide will be continually produced during electrolysis at high current densities, the net effect is the same as though an anode which is a good catalyst for hydrogen peroxide decomposition were employed (20). The lower oxides of nickel do not decompose hydrogen peroxide appreciably.

with those electrodes which are the poorest catalysts for the decomposition of hydrogen peroxide. The oxidation of chromic salts to chromates (reaction V) on the other hand, is not only brought about by active oxygen (reaction (d)), but the presence of hydrogen peroxide, as already explained, tends to reduce the chromate ions to chromic ions (reaction (b)) and so decreases the oxidation efficiency. The best yields of chromate are thus obtained, as seen in table 6, with anodes which are the most effective catalysts for hydrogen peroxide decomposition.

There is another aspect of the influence of anode material to which reference must be made: namely, the possibility that it may behave as a catalyst for the reaction between the depolarizer and active oxygen. The action of the latter on the electrode material may produce a peroxide which acts as a catalytic intermediate compound, suffering reduction by the depolarizer and subsequent re-oxidation by the oxygen produced when the hydrogen peroxide is decomposed. This type of catalytic action is probably operative in the oxidation of chromic salts to chromate, and of iodate to periodate, the anode material acting as an oxygen carrier. It will be

TABLE 7

Current efficiencies for ethane formation with platinized platinum anode

| Poison..... | None | 0.1 M Hg(CN) ₂ | 0.1 M KCN | 0.1 M NaF |
|------------------------------|------|---------------------------|-----------|-----------|
| Efficiency, in per cent..... | 3 | 14 | 13 | 10 |

seen from table 6 that the efficiency of a gas-carbon anode for the oxidation of chromic ions is somewhat less than would be expected from its ability to decompose hydrogen peroxide; carbon is, however, a poor oxygen carrier, and the oxidation efficiency must inevitably be small.

It has been recorded that the efficiency of a platinized platinum anode for the oxidation of thiosulfate is unexpectedly high because of the poisoning action of the depolarizer; it is possible, in an analogous manner, deliberately to poison an electrode and so increase its efficiency for reactions in which hydrogen peroxide is the effective oxidant. The current efficiencies in table 7 were obtained in the electrolysis of a solution of *N* potassium acetate and *N* acetic acid with a platinized platinum anode at an apparent current density of 0.25 ampere per square centimeter, in the presence of various poisons. Although the efficiencies are not very high, the catalytic poisons are seen to bring about a definite increase in the yield of ethane. A more striking effect was observed when the platonic chloride solution used for platinizing the anode was made 0.01 *M* with respect to mercuric chloride. With this electrode the efficiency for ethane formation was found to be 42 per cent, as compared with 3 per cent for an anode prepared

in the same manner from a solution free from mercuric salt. As far as could be seen with the naked eye, the appearance of the poisoned and unpoisoned electrodes was the same.

One of the most striking achievements of the hydrogen peroxide theory is its ability to explain the effects of previous anodic and cathodic polarization on a platinum anode. It had been recorded by Friessner (16) that previous anodic polarization of a platinum anode increased, whereas cathodic polarization decreased, the amount of dithionate produced in the electrolytic oxidation of sulfite. Similarly Foerster and Piguët (15) noted that anodic pre-polarization favored the formation of ethane in the electrolysis of acetate solutions. These conclusions have been confirmed (19, 20), and the results in table 8 may be quoted to illustrate the nature of the effects in the oxidation of sulfite to dithionate (reaction II) at a smooth platinum anode and of acetate to ethane (reaction III) at a platinized platinum anode. The figures for the efficiency of the conversion of chromic

TABLE 8
Current efficiencies with pre-polarized platinum anodes

| | CURRENT EFFICIENCIES | | |
|-----------------------------|----------------------|-----------------|-----------------|
| | Reaction II | Reaction III | Reaction V |
| | <i>per cent</i> | <i>per cent</i> | <i>per cent</i> |
| Anodically polarized..... | 33 | 36 | 43 |
| Untreated..... | 22 | | 53 |
| Cathodically polarized..... | 12 | 3 | 97 |

ions to chromate (reaction V) at platinized platinum are also given (23). It is seen that the results in the third column indicate a behavior which is the reverse of that found in the oxidation of sulfite and acetate ions; previous anodic polarization of the electrode is detrimental to the formation of chromate, whereas cathodic pre-polarization is advantageous.

The explanation of these results is provided by the observation of Spitalsky and Kagan (41) that anodic polarization of platinum decreases its catalytic power for the decomposition of hydrogen peroxide, whereas cathodic polarization greatly enhances it. Where anodic oxidation is brought about by the direct action of hydrogen peroxide, therefore, as is believed to be the case for reactions II and III, anodic pre-polarization should increase and cathodic polarization decrease the oxidation efficiency, as actually observed. On the other hand, where the presence of hydrogen peroxide tends to reduce the product, as in the oxidation of chromic salts to chromate in acid solution (reaction V), the effects of anodic and cathodic pre-polarization are reversed, as shown in table 8.

D. Effect of catalysts for hydrogen peroxide decomposition

Mention has been made in the section dealing with the origin of the theory of the anodic formation of hydrogen peroxide that catalysts for its decomposition diminish very markedly the efficiency of the electrolytic oxidation of thiosulfate to tetrathionate (table 2). In view of the results recorded above for reactions of different types, it is to be expected that the same effect should be observed for all reactions of type (a), in which hydrogen peroxide is the active oxidizing agent. When the oxidation product is decomposed by the peroxide, however, as in the formation of chromate in acid solution, the addition of catalysts should increase the net efficiency of the electrolytic process. The experimental results are again in harmony with expectation: the presence of lead, silver, manganous, cupric, cobalt, and ferrous or ferric ions diminishes the efficiency for the

TABLE 9
Effect of catalysts for hydrogen peroxide decomposition

| CATALYST | OXIDATION OF POTASSIUM ETHYL MALONATE | CATALYST | OXIDATION OF ACID CHROMIC SULFATE |
|---------------------------------------|--|---------------------------------------|---|
| | <i>per cent</i> | | <i>per cent</i> |
| None..... | 78 | None..... | 1 |
| 0.01 <i>M</i> Ag ⁺ | 50 | 0.01 <i>M</i> Ag ⁺ | 97 |
| 0.01 <i>M</i> Fe ⁺⁺⁺ | 49 | 0.01 <i>M</i> Fe ⁺⁺⁺ | 2 |
| 0.01 <i>M</i> Co ⁺⁺ | 45 | 0.01 <i>M</i> Co ⁺⁺ | 8 |
| 0.01 <i>M</i> Cu ⁺⁺ | 38 | 0.01 <i>M</i> Cu ⁺⁺ | 2 |
| 0.01 <i>M</i> Mn ⁺⁺ | 37 | 0.01 <i>M</i> Mn ⁺⁺ | 7 |
| 0.01 <i>M</i> Pb ⁺⁺ | 27 | PbSO ₄ (saturated)..... | 70 |

oxidation of sulfite to dithionate (19), of acetate to ethane (20), and of potassium ethyl malonate to diethyl succinate (26), as well as that for the oxidation of thiosulfate to tetrathionate (table 2). The conversion of chromic ions to chromate in acid solution, on the other hand, is favored by the presence of catalysts for hydrogen peroxide decomposition. The efficiencies observed in the oxidation of an approximately neutral solution of potassium ethyl malonate and of acidified chromic sulfate, at smooth platinum anodes, are quoted in table 9; the opposite influences of the catalysts in reactions of different types are here apparent. Complete parallelism between the two sets of results is not to be expected, since in the second reaction, the oxidation of chromic ions to chromate, the added catalysts have a second rôle to play in acting as carriers for the oxidation by oxygen, and in this respect, as found by direct experiment, they differ considerably (23).

In general the effectiveness of the metallic ions for hydrogen peroxide

decomposition follows the order Pb, Ag, Mn, > Cu, Co, Fe, and their influence on electrolytic oxidation processes in which hydrogen peroxide is the effective oxidant usually follows a similar order. Since, in most cases, the catalytic activity of the metallic ion is bound up with the possibility of the formation of a metallic peroxide, it follows that their influence should be greater in neutral than in acid solution, and this is usually found to be the case. Furthermore, any factor which tends to hinder the accumulation of the active substance in the vicinity of the anode, such as high current density leading to vigorous gas evolution, lessens their effects.

E. Influence of acidity and alkalinity

Since hydrogen peroxide is more stable in acid than in alkaline solution, it follows that when electrolytic oxidation is to be attributed to the peroxide, the efficiency should be highest in acid solution and should decrease as the pH of the medium is made larger. The converse should hold where

TABLE 10

Effect of acidity and alkalinity on chromate formation at a platinum anode

| MEDIUM | EFFICIENCY |
|--------------------------------|-----------------|
| | <i>per cent</i> |
| 0.5 N sulfuric acid..... | 1 |
| Water..... | 63 |
| 0.5 N potassium hydroxide..... | 77 |

the presence of hydrogen peroxide tends to decrease the oxidation efficiency. Results of the first kind have already been quoted in table 3, for the electrolytic oxidation of thiosulfate ions, and a similar effect has been found in the conversion of sulfite to dithionate over the pH range of 7 to 13, when the efficiency decreases from 33 to 17 per cent. Another factor is operative in this case to which reference is made below. The anodic oxidation of chromic salts to chromate, in agreement with the arguments presented above, takes place more efficiently in alkaline than in acid solution, as is clear from table 10. Somewhat similar results have been recorded in the oxidation of iodate to periodate.

Where the oxidation process involves direct interaction between hydrogen peroxide and the anion of a weak acid, then in addition to the stability of the peroxide it is necessary to take into consideration the fact that the concentration of the ions of depolarizer decreases as the solution becomes more acid. This factor will tend to diminish the oxidation efficiency as the pH decreases, and thus will oppose the increase which should result from the greater stability of the hydrogen peroxide. As a consequence of

these two opposing influences, the efficiency of the anodic oxidation may be expected to increase to a maximum and then to diminish as the pH is increased: results of this kind have been obtained with solutions of sulfite (19), acetate (20), and ethyl malonate ions (26), as shown by the data in table 11. The values for the oxidation of sulfite were obtained with 0.025 *M* potassium sulfite in various buffer mixtures at a current density of 0.001 ampere per square centimeter. Except for the most alkaline, the acetate solutions were prepared from potassium acetate and acetic acid, the total concentration being 2 *N* in each case. The solution of pH 11 was prepared by adding a small quantity of ammonia to 2 *N* potassium acetate; the current density was 0.05 ampere per square centimeter. The malonate solutions consisted of mixtures of potassium ethyl malonate and hydrogen

TABLE 11
Variation of current efficiency with pH of the electrolyte

| SULFITE IONS | | ACETATE IONS | | ETHYL MALONATE IONS | |
|--------------|-----------------|--------------|-----------------|---------------------|-----------------|
| pH | Efficiency | pH | Efficiency | pH | Efficiency |
| | <i>per cent</i> | | <i>per cent</i> | | <i>per cent</i> |
| 1 | 4 | 2.3 | 67 | 1.4 | 70 |
| 3 | 11 | 4.3 | 70 | 2.9 | 75 |
| 5 | 24 | 4.7 | 77 | 3.5 | 74 |
| 7 | 33 | 5.2 | 74 | 4.8 | 74 |
| 9 | 33 | 9.5 | 71 | 7.0 | 70 |
| 11 | 26 | 11 | ca. 50 | 8.3 | 64 |
| 13 | 17 | | | 10 | 59 |

ethyl malonate of 2 *N* total concentration, the two alkaline solutions containing in addition 0.1 *M* potassium bicarbonate and carbonate, respectively; a current density of 0.5 ampere per square centimeter was employed. All the measurements were made with a smooth platinum anode at room temperature.

F. Influence of temperature

The rate of decomposition of hydrogen peroxide increases with rise of temperature, and hence it is to be expected that anodic oxidations brought about by the peroxide should decrease in efficiency as the temperature is raised. Conversely, anodic oxidations due to active oxygen and hindered by hydrogen peroxide should show increasing efficiency with rise of temperature. These points are illustrated by the figures in table 12 for the efficiency of the formation of diethyl succinate from ethyl malonate ions (26), and of chromate from an acidified solution of chromic sulfate (23);

a smooth platinum anode was used in each case, and the current densities were 0.5 ampere per square centimeter and 0.01 ampere per square centimeter, respectively. The efficiency for the oxidation of a 20 per cent solution of potassium acetate to ethane also decreases from 83 per cent at 0°C. to 12 per cent at 90°C. (38), as is to be anticipated, but the formation of periodate is also said to be favored by low temperatures (30); this result is unexpected in view of the probable nature of the anodic process, but the subject requires further investigation. It must be mentioned that other temperature-variable factors, in addition to those mentioned above, may have an important influence on the anodic oxidation efficiency. Rise of temperature may increase the rate of the chemical reactions, for example, between the depolarizer and active oxygen, but it may also facilitate the liberation of oxygen gas in the molecular form and thereby diminish the tendency for oxidation to occur. The operation of these factors may lead

TABLE 12

Influence of temperature on the formation of diethyl succinate and of chromate

| TEMPERATURE | SUCCINATE FORMATION | CHROMATE FORMATION |
|-------------|---------------------|--------------------|
| °C. | <i>per cent</i> | <i>per cent</i> |
| 10 | 74 | |
| 20 | | 1 |
| 30 | 63 | 21 |
| 50 | 56 | 47 |
| 60 | | 60 |
| 70 | 37 | 77 |
| 90 | 22 | 77 |

to results which are difficult to analyze: for example, the oxidation of alkaline solutions of formate ions is favored by increase of temperature at iron and nickel anodes, but at a smooth platinum anode there is a marked decrease of efficiency, especially in the early stages of electrolysis (14). It appears, however, in agreement with the hydrogen peroxide theory, that, in general, increase of temperature facilitates those reactions involving oxidation by active oxygen, but sometimes so many influences are at work that it is not possible to interpret the results in a simple manner.

G. Effect of current density

When the hydrogen peroxide formed at the anode takes part almost wholly in one oxidation reaction, the current efficiency for oxidation should be greatest at low current densities, for at large current densities the concentration of hydrogen peroxide at the anode is high and its rate of spon-

taneous decomposition is considerable. These conditions appear to apply to the oxidation of thiosulfate, where the efficiency, as shown in table 13, for a 0.025 *M* solution at pH 7, decreases with increasing current density at a smooth platinum anode.

The position is, however, not always so simple as implied above and as apparently exists in the anodic oxidation of thiosulfate. If the reaction between hydrogen peroxide and the depolarizer does not occur very rapidly, it may be necessary for there to be an appreciable concentration of the former for the process to take place with reasonable efficiency; this is probably the case in the oxidation of acetate ions to ethane, for which the

TABLE 13
Efficiency of oxidation of thiosulfate at different current densities

| CURRENT DENSITY $\times 10^3$ | EFFICIENCY |
|-------------------------------|-----------------|
| <i>amperes per sq. cm.</i> | <i>per cent</i> |
| 0.2 | 90 |
| 0.4 | 88 |
| 1.0 | 85 |

TABLE 14
Efficiency for oxidation of acetate ions to ethane at different current densities

| CURRENT DENSITY | EFFICIENCY |
|----------------------------|-----------------|
| <i>amperes per sq. cm.</i> | <i>per cent</i> |
| 0.005 | 52 |
| 0.025 | 71 |
| 0.05 | 77 |
| 0.25 | 89 |
| 0.5 | 89 |

data are given in table 14. They were obtained with a solution containing *N* acetic acid and *N* potassium acetate using a smooth platinum anode.

In some cases, both the factors mentioned above seem to be operative, and the efficiency increases to a maximum and then decreases as the current density is raised; this is the case, for example, with the formation of diethyl succinate from potassium ethyl malonate, for which there is an optimum current density of about 0.12 ampere per square centimeter when an electrolyte consisting of *M* potassium ethyl malonate and *M* hydrogen ethyl malonate is used. Where an anodic oxidation is brought about by active oxygen, a low current density is usually favorable, the dominating factor being probably the rate at which the electrode material can catalyze the reaction.

H. Influence of depolarizer concentration

No matter what is the effective oxidant, an increase of depolarizer concentration should result in an increase of efficiency, and this is generally found to be the case. A number of illustrations are recorded in table 15, the concentrations being in terms of molarity: *C* represents the total concentration, and *E* the efficiency per cent for the formation of the main product. A small concentration of depolarizer will result in the decomposition of a larger proportion of the hydrogen peroxide, and therefore a general oxidation process with active oxygen, of type (*d*), may be favored. As will be seen shortly, this phenomenon occurs in the electrolysis of organic acids and their salts, e.g., acetic acid and acetates, when the formation of ethane is replaced by that of methyl alcohol. If the concentration of depolarizer is made too low, the oxidation reactions, whether

TABLE 15

Influence of concentration of depolarizer on oxidation efficiencies at a platinum anode

| THIOSULFATE IONS | | SULFITE IONS | | ACETATE IONS | | ETHYL MALONATE IONS | | CHROMIC IONS | |
|------------------|----------|--------------|----------|--------------|----------|---------------------|----------|--------------|----------|
| <i>C</i> | <i>E</i> | <i>C</i> | <i>E</i> | <i>C</i> | <i>E</i> | <i>C</i> | <i>E</i> | <i>C</i> | <i>E</i> |
| 0.02 | 75 | 0.025 | 36 | 0.2 | 44 | 0.2 | 30 | 0.02 | 20 |
| 0.05 | 85 | 0.10 | 37 | 1.0 | 64 | 0.5 | 68 | 0.05 | 36 |
| | | 0.20 | 37 | 2.0 | 77 | 1.0 | 70 | 0.1 | 53 |
| | | | | 4.0 | 77 | 2.0 | 74 | 0.2 | 66 |
| | | | | | | 4.0 | 78 | | |

brought about by hydrogen peroxide or active oxygen, will be so slow that oxygen evolution may take place.

I. Influence of foreign anions

It has been found that in the electrolysis of salts of some organic acids the presence of inert inorganic salts tends to inhibit the main anodic reaction and leads to the formation of an alternative product; the effect is particularly marked in acid solutions. For example, in the electrolysis of an aqueous solution of acetic acid a high efficiency for ethane formation is observed, but if an inorganic acid or the potassium salt of an inorganic acid is added, the efficiency is greatly decreased⁴ and methyl alcohol is

⁴ Some textbooks of organic chemistry state that ethane can be obtained by electrolysis of aqueous acetic acid solutions, whereas others say that it is not formed in this manner; the negative results obtained by many workers are to be explained by the addition of some free mineral acid, e.g., sulfuric acid, in order to increase the conductivity of the feebly conducting acetic acid solution. In doing so the conditions have been unwittingly changed from those requisite for ethane formation to those resulting in the production of methyl alcohol.

formed (Hofer-Moest reaction) instead of ethane. As a consequence of experiments (20), the results of which are reproduced in table 16, it is clear that the effect is related to the mobility of the added anion; it is more marked the greater the speed of the ion.

This interesting phenomenon, which is also shown in the electrolysis of acid-ester salts (26), is readily explicable on the basis of the hydrogen peroxide theory. For the formation of ethane to occur at a reasonable rate, a fairly high concentration of acetate ions is necessary in the vicinity

TABLE 16

Influence of 0.01 N potassium salts on the formation of ethane from 2 N acetic acid at a platinum anode

| ADDED SALT | EFFICIENCY | MOBILITY OF ANION |
|--|-----------------|-------------------|
| | <i>per cent</i> | |
| None..... | 71 | |
| KF..... | 30 | 47 |
| KClO ₄ | 20 | 64 |
| KNO ₃ | 19 | 62 |
| KH ₂ PO ₄ | 17 | |
| KCl..... | 5 | 65 |
| K ₂ SO ₄ | 3 | 69 |
| K ₃ Fe(CN) ₆ | 0 | 97 |

TABLE 17

Effect of added salt at various current densities

| CURRENT DENSITY | EFFICIENCY | | DECREASE OF EFFICIENCY |
|----------------------------|-----------------|---------------------------------------|------------------------|
| | No added salt | 0.02 N K ₂ SO ₄ | |
| <i>amperes per sq. cm.</i> | <i>per cent</i> | <i>per cent</i> | |
| 0.05 | 43 | 34 | 9 |
| 0.2 | 76 | 42 | 34 |
| 0.5 | 70 | 11 | 59 |

of the anode to react with the hydrogen peroxide produced there. Some of these ions may arrive at the anode by diffusion from the main body of the solution, but in the acid electrolyte this process will be very slow, since the acid is only weakly dissociated and the bulk concentration of ions is low. The majority of the acetate ions will be brought up to the anode in transporting the current, and at not too high current densities will give a concentration sufficient for good synthesis to occur. If, now, an inorganic electrolyte is added, the foreign anion will take over to a considerable extent the transport of current to the anode and therefore interrupt the supply of acetate ions; the concentration of these ions near the electrode

will therefore fall, and hence the efficiency should decrease. The effect should be related to the mobility of the added anion, as is found to be the case. If the view put forward is correct, it would be expected that the influence of added salts should be greatest at high current densities, since here ordinary diffusion to the electrode will supply only a negligible fraction of the depolarizer ions required. This is borne out by the figures in table 17 for the synthesis of diethyl succinate by the electrolysis of 2 *M* ethyl hydrogen malonate with and without potassium sulfate added (26).

In solutions of salts of the organic acids it is to be expected that the effect of added anions will be less, since the concentration of depolarizer ions is much greater, and hence ordinary diffusion to the electrode is more marked, and the ions can also compete effectively with foreign anions in carrying the current. This is found to be true in practice: thus with *N* potassium acetate and *N* acetic acid and the same current density as was employed in the experiments recorded in table 16, the efficiency of ethane formation was only reduced from 77 to 42 per cent by the presence of 0.2 *N* potassium sulfate.

J. Electrode potential phenomena

No mention has hitherto been made of the interpretation of electrode potentials by means of the theory of the anodic formation of hydrogen peroxide; this important aspect of electrolytic oxidation must now be considered. The essential postulate is that the measured potentials are set up *indirectly* by electromotively active substances formed at the anode, and these potentials may have no direct connection with the nature of the products. The electromotively active material may be either oxygen, arising from the decomposition of the hydrogen peroxide, or discharged radicals produced by the action of the latter on the depolarizer; these two possibilities will be considered separately.

- (I) The only electromotively active substance is oxygen arising from the decomposition of the hydrogen peroxide

It is well known that although the equilibrium between oxygen gas and hydroxyl ions represented by the equation



is generally not strictly reversible, a given concentration of oxygen nevertheless gives rise to a more or less definite potential. It may be assumed, therefore, that the potential of an anode, in the present circumstances, will be determined by the amount of oxygen accumulated on the electrode. When oxygen is added to a virgin platinum anode, two stages of potential are observed (6): a lower one, less than 1 volt, corresponding to the

formation of a layer of oxygen atoms on the platinum surface, and a higher corresponding to oxygen evolution. The actual values of the potentials are dependent, of course, on the hydroxyl-ion concentration of the solution. It is to be expected, therefore, that for an electrolytic oxidation in which hydrogen peroxide is the effective agent and the potential is due to the accumulation of oxygen at the anode, two stages of potential should be observed, a lower one indicating the covering of the platinum surface with oxygen atoms and a higher one corresponding to very slow oxygen gas evolution. If the oxidation process is efficient at low current densities, or if the oxygen itself can react with the depolarizer, the lower potential stage will be prolonged; this is particularly the case in the oxidation of sulfite ions. Any factor which tends to lengthen the period required for the saturation of the surface with oxygen, such as low current density or a platinized surface, should increase the quantity of electricity which must be passed before the potential rise from the first to the second stage is observed. On the other hand, factors tending to increase the rate of oxygen formation, e.g., the addition of catalysts for hydrogen peroxide decomposition, should shorten the lower potential stage; in these cases the oxidation efficiency is also low, as explained previously. A catalytic poison, such as mercuric cyanide, which is strongly adsorbed by platinum, may eliminate almost entirely the adsorption of oxygen corresponding to the lower stage of potential; the potential should then rise rapidly to the higher stage, but in these circumstances there is no reason why the oxidation efficiency should be appreciably affected. The phenomena considered are very elegantly shown in the electrolysis of thiosulfate solution (18). In figure 1 are reproduced the curves of anode potential plotted against quantity of electricity passed, for 0.025 *M* thiosulfate solution in pH 7 buffer at various currents with a smooth platinum anode of area approximately 55 sq. cm.; the oxygen evolution potential for the buffer alone at the lowest current is also given. The two potential stages are clearly seen, and it is observed that as the current is increased, leading to more rapid decomposition of the anodic hydrogen peroxide, the lower stage is shortened; the higher potential is seen to be rather less than the oxygen evolution potential given and corresponds undoubtedly to very slow oxygen evolution.

The effect of catalysts for hydrogen peroxide decomposition is shown in figure 2. The broken curve is for 0.025 *M* thiosulfate at pH 7 with a current of 0.01 ampere, while the other curves are for the same solution containing copper sulfate, ferrous sulfate, and solid manganese dioxide, respectively; the quantities added are as given in table 2. As expected, the lower potential stage is shortened and the higher potential raised corresponding to a greatly increased rate of oxygen formation.

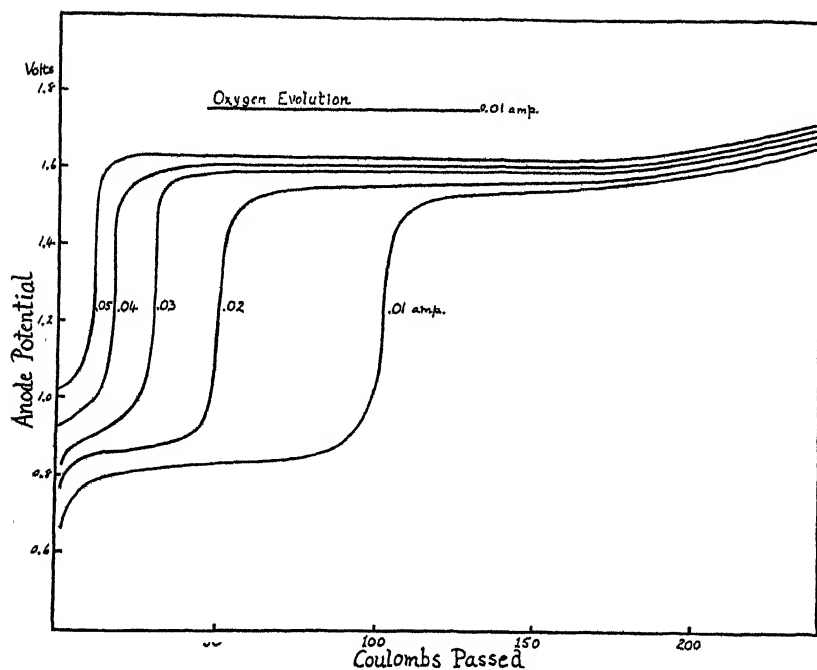


FIG. 1. Anode potential plotted against quantity of electricity passed for 0.025 *M* thiosulfate solution in pH 7 buffer at various currents with a smooth platinum anode of area approximately 55 sq. cm.

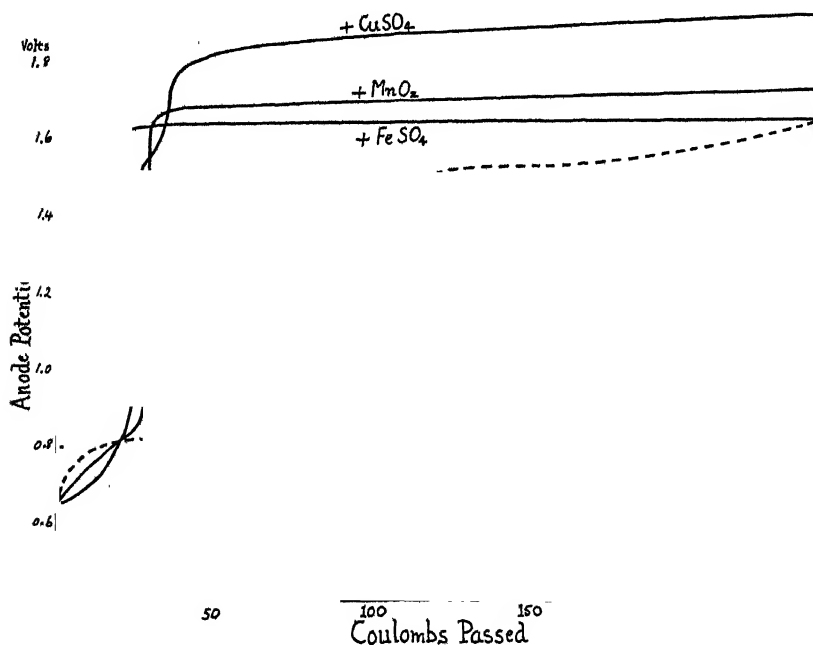


FIG. 2. The effect of catalysts for hydrogen peroxide decomposition

Figure 3 shows the inhibition of the first potential stage by mercuric cyanide. The broken curve is for thiosulfate alone under the same conditions as before, while curves I, II, and III are those observed with solutions containing 0.001 *M*, 0.0001 *M*, and 0.00001 *M* mercuric cyanide, respectively. It is seen that the lower potential stage is shortened, but the higher potential is unaffected; this is to be expected, since the poison does not influence the oxidation efficiency and therefore the rate of oxygen formation.

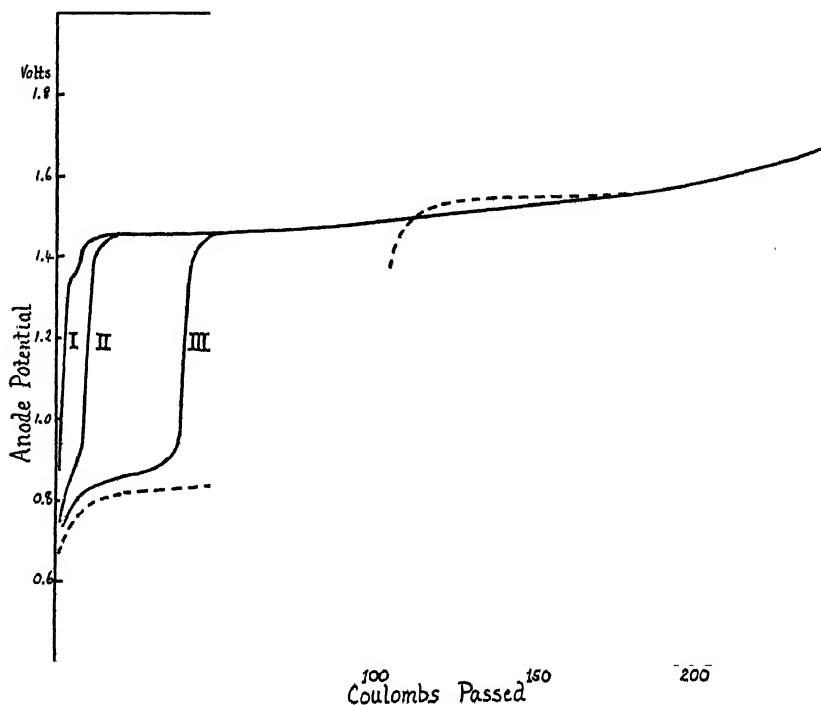


FIG. 3. The inhibition of the first potential stage by mercuric cyanide. Broken curve, thiosulfate alone. Curves I, II, and III were obtained with solutions containing 0.001 *M*, 0.0001 *M*, and 0.00001 *M* mercuric cyanide, respectively.

Similar observations have been made in the electrolytic oxidation of sulfites (19), methyl alcohol (32, 42), formaldehyde (32, 42), and ethyl alcohol (28). Where an electrolytic oxidation is carried out at high current densities, or the oxidation process is not very efficient, the rate of formation of free oxygen is naturally high; the lower potential stage may then be so short as not to be observable, and the anode potential will be in the vicinity of that for oxygen evolution from the commencement of electrolysis.

With anodes other than platinum,⁵ there does not appear to be a lower

⁵ It is possible that some of the other metals of the platinum group, e.g., rhodium or iridium, may behave similarly to platinum.

potential stage corresponding to oxygen adsorption, and thus the anode potential in electrolytic oxidation is usually in the neighborhood of that requisite for oxygen evolution.

- (II) Hydrogen peroxide reacts with the depolarizer giving discharged radicals capable of setting up a potential with respect to the corresponding ions in solution

Two possibilities may be distinguished:

(a) *The liberated radicals may set up a potential below that of oxygen evolution.* This is the case, for example, in the electrolysis of halides (21). The hydrogen peroxide will react with the halide to liberate free halogen, which sets up its own potential against the ions in solution. (At this potential, of course, direct discharge of some halide ions may take place.) The oxygen arising from the simultaneous decomposition of the peroxide accumulates on the anode. At first it goes to form the adsorbed oxygen layer, and since the potential of this is below the halogen potential, it is not apparent. Eventually, however, the electrode surface becomes saturated with oxygen and the potential rises to that for slow oxygen evolution. Any factor tending to increase the rate of decomposition of the hydrogen peroxide causes the jump of potential to occur sooner. These points are well brought out by the curves in figure 4, giving the potentials against quantity of electricity passed for the electrolysis of chloride solutions under various conditions (21). The results were obtained with a rotating, smooth platinum anode, of approximately 55 sq. cm. area. Owing to the presence of an electrical resistance between the anode and the tip of the siphon connecting it to the calomel reference electrode, all the potentials recorded are higher than the true values, but the time elapsing before the sudden rise of potential occurs, which is the phenomenon of immediate interest, remains unaffected. The curves in figure 4A show the variation with time of the anode potential in a 0.1 *N* hydrochloric acid solution electrolyzed with currents of 0.1, 0.25, and 0.5 ampere, respectively. It is seen that the higher the value of the current used, the smaller is the quantity of electricity that has to be passed before the sudden rise of potential occurs. The effect of varying the hydrochloric acid concentration is seen in figure 4B; the anode potential-time curves are for 0.05, 0.1, and 0.2 *N* solutions electrolyzed with a constant current of 0.25 ampere; it is evident that decrease of concentration favors the polarization. Figure 4C shows the effect of varying the hydrogen-ion concentration at constant chloride-ion concentration; the curves are for (a) *N* sodium chloride in 0.1 *N* sodium hydroxide, (b) *N* sodium chloride, and (c) 0.9 *N* sodium chloride in 0.1 *N* hydrochloric acid, a current of 0.25 ampere being used in each case. As would be expected, the onset of polarization is

markedly favored by alkalinity of the electrolyte. The effect of catalysts for hydrogen peroxide decomposition is shown in figure 4D; the solutions were prepared from 0.1 *N* hydrochloric acid and in addition were either 0.001 *M* with respect to manganous or ferrous chlorides or contained 0.5 g. of powdered manganese dioxide, precipitated silver, or animal charcoal

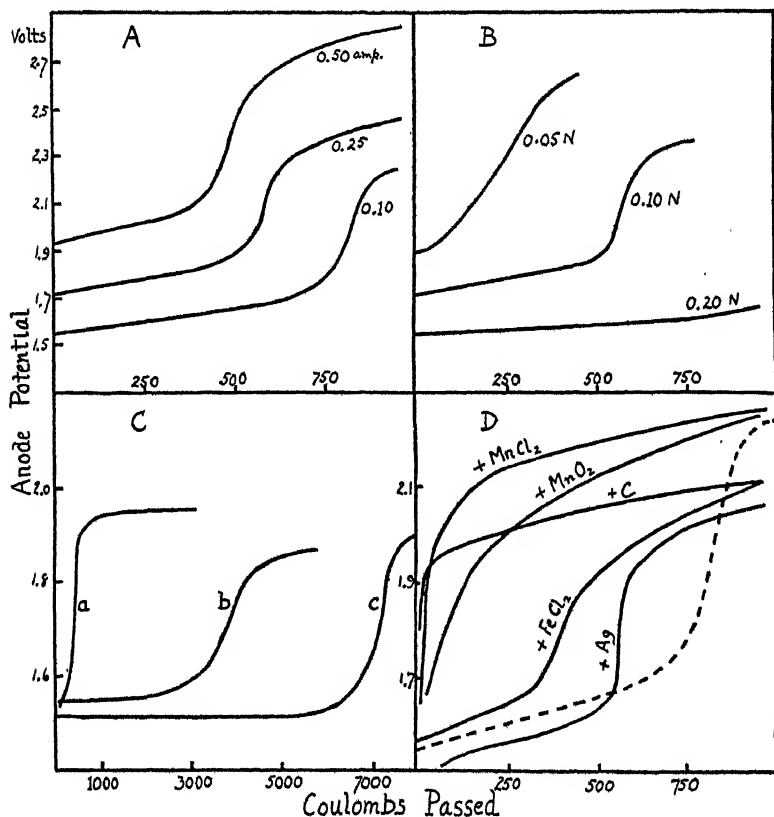


FIG. 4. (A) The variation with time of the anode potential in a 0.1 *N* hydrochloric acid solution electrolyzed with currents of 0.1, 0.25, and 0.5 ampere. (B) The effect of varying the hydrochloric acid concentration. (C) The effect of varying the hydrogen-ion concentration at constant chloride-ion concentration. (D) The effect of catalysts for hydrogen peroxide decomposition.

suspended in 100 ml. of electrolyte. The influence of the added substances in facilitating the onset of polarization is very marked. Solutions of bromides and iodides were found to behave similarly to chlorides but, as would be expected since hydrogen peroxide reacts more readily with the former substances, polarization did not take place so readily as in chloride solutions.

(b) *The liberated radicals may set up a potential above that of oxygen evolution.* This is the case, for example, in the electrolysis of acetates and acid-ester salts. The potential at which the Kolbe reaction takes place is about 2.4 volts⁶ and that for the Brown-Walker synthesis is about 2.8 volts, while the oxygen evolution potentials for the same solutions are about 2.0 volts or less. These figures provide a very awkward problem for the old theories of electrolytic oxidation: since the processes of electrosynthesis require a higher potential than that for oxygen evolution, how is it, if the anode potential is the determining factor, that these processes ever take place? One would expect that, in aqueous solution, the requisite potential could never be attained, oxygen evolution taking place preferentially. The hydrogen peroxide theory, however, encounters no such anomaly; there is no reason why hydrogen peroxide formed *irreversibly* at the anode should not give rise by chemical reaction to electromotively active radicals capable of setting up potentials considerably higher than those for oxygen evolution. As long as the reaction is maintained, therefore, a high potential will be observed. If, however, the decomposition of the hydrogen peroxide to give oxygen is favored, e.g., by introducing catalysts, the synthetic reaction will be largely inhibited and the concentration of the radicals at the anode due to it will fall considerably; the potential corresponding to the electrosynthesis will therefore decrease and may fall below that for oxygen evolution. The latter process will then determine the observed potential. These points are well illustrated by the curves in figure 5 for the electrolysis of ethyl malonate ion solutions under various conditions. The electrolyte used consisted of *M* potassium ethyl malonate and *M* hydrogen ethyl malonate, and all observations were at room temperature (26). Curve A is the current density-potential curve for smooth platinum, curve B that for platinized platinum, curve C that for gold, and curve D that for lead dioxide; the broken curve (E) is for smooth platinum in a phthalate buffer of the same pH as the electrolyte, and indicates approximately what should be the ordinary oxygen evolution potential for the malonate solution if no electrolytic oxidation processes

⁶ Shukla and Walker (40) recorded the potential of the Kolbe synthesis as 2.14 volts; this referred, however, to the first break in the current density-potential curve, and not to the potential actually observed when the synthesis was proceeding with good efficiency at high current density. Glasstone and Hickling (20), using the commutator-extrapolation method, obtained appreciably higher values, but the results were admittedly only approximate owing to the very rapid fall of potential on switching off the polarizing current. Unpublished observations by Hickling and Westwood, using a new method (25) for the measurement of polarization potentials, give a value of 2.42 volts for *N* acetic acid + *N* potassium acetate independent of current density over the range 0.05 to 1.5 amperes per square centimeter.

took place. It is seen that when the formation of diethyl succinate takes place with high efficiency, as at a smooth platinum anode (curve A), the potential is about 2.8 volts, but when the synthesis is inhibited by using

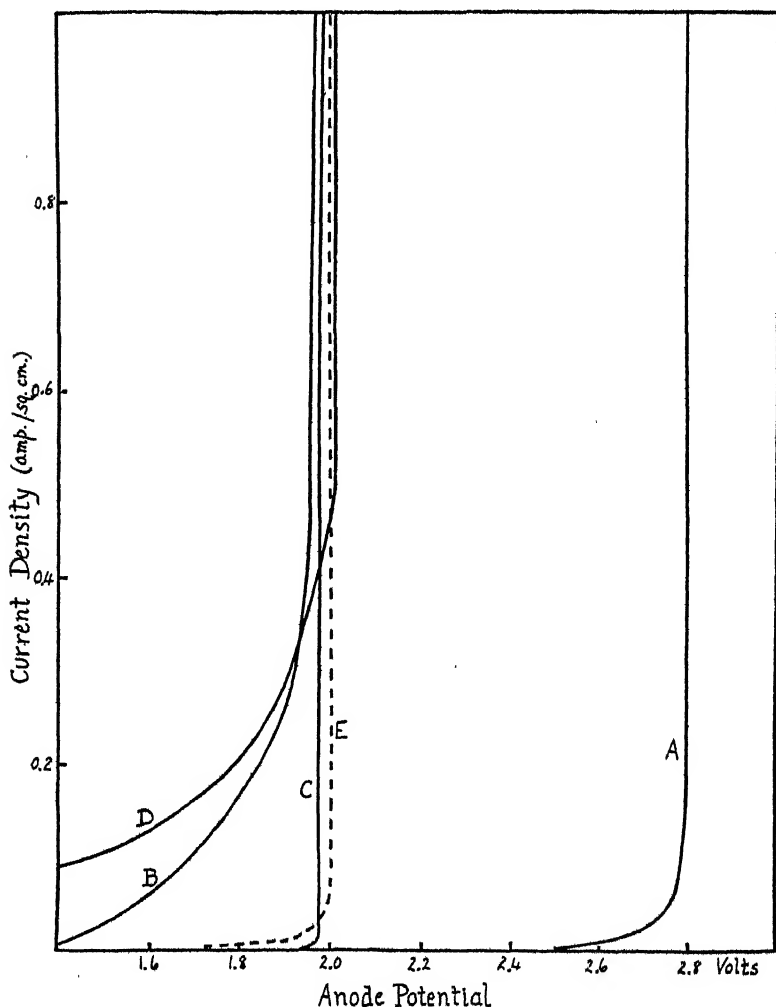


FIG. 5. The electrolysis of ethyl malonate ion solutions under various conditions. Current density-potential curves for smooth platinum (curve A), for platinized platinum (curve B), for gold (curve C), for lead dioxide (curve D), and for smooth platinum in a phthalate buffer of the same pH as the electrolyte (curve E).

anodes which are good catalysts for hydrogen peroxide decomposition (curves B, C, and D), the potential drops to the region of oxygen evolution, at about 2 volts. It may even drop somewhat lower, at small current

densities, when oxygen depolarization can occur at some anodes, leading to alternative anodic oxidation products.⁷

K. Detection of hydrogen peroxide at the anode

If hydrogen peroxide is the primary product at the anode in the electrolysis of aqueous solutions, as maintained by the authors, it might be expected that the hydrogen peroxide could be detected analytically. This has been done in certain cases in the electrolysis of sulfuric acid and salts of organic acids, but there is the possibility that it may arise here by secondary reactions. Riesenfeld and Reinhold (36), however, were able to detect small quantities of hydrogen peroxide at the anode in the electrolysis of potassium hydroxide solution at low temperatures; here there appears to be no possibility of a secondary reaction. More recently Rius (37) has shown that very appreciable quantities of hydrogen peroxide may be obtained at the anode in the electrolysis of potassium hydroxide solution at low temperatures, if fluoride is present. The difficulty of detecting hydrogen peroxide at an anode is attributed by the writers to the fact that it is formed in a layer of high local concentration, on a metal surface, probably locally heated, which is a good catalyst for its decomposition. Under these conditions the rate of decomposition of the peroxide will be extremely high. If an electrolysis could be carried out without any anode material in contact with the electrolyte, then it should be possible to obtain hydrogen peroxide in quantity. In support of this view it has been shown (22) that if various solutions are electrolyzed by passing a discharge from an anode placed in an evacuated space above the surface of the electrolyte, then hydrogen peroxide is formed in quantities approximating those required by Faraday's laws. It should be emphasized that the peroxide is not merely the result of the high tension electrical discharge, for it is not obtained when the electrode in the gas space is made the cathode.

IV. DIFFICULTIES AND CRITICISMS OF THE HYDROGEN PEROXIDE THEORY

It will be clear from the preceding pages that, provided the reactions of hydrogen peroxide and of active oxygen on the depolarizer are known and the possibilities of interaction with the oxidation product are taken into account, the more important features of many electrolytic processes can be explained. There is, however, one important difficulty: it is not always possible to imitate anodic oxidations quantitatively using hydrogen peroxide as chemical oxidizing agent. By the action of hydrogen peroxide

⁷ The application of reaction rate theory to electrode potential phenomena (H. Eyring, S. Glasstone, and K. J. Laidler: *J. Chem. Phys.* **7**, 1053 (1939)) may necessitate some modification of the interpretation given above.

on a 0.025 *M* solution of sodium thiosulfate in a phosphate buffer at pH 7, it was found that 82 per cent of the thiosulfate was oxidized, 74 per cent being converted into tetrathionate and 8 per cent into sulfate (18), in close agreement with the results of anodic oxidation, but treatment of sulfite solution with hydrogen peroxide under various conditions gave not more than 2 per cent of dithionate, compared with yields of about 30 per cent obtained electrolytically. It appears that the difficulty of duplicating chemically the anodic process is connected with the possibility that the hydrogen peroxide may take part in two different reactions. For example, in the oxidation of sulfite reactions of types (a) and (d) can occur simultaneously, the first leading to dithionate and the second to sulfate; it is probable that the latter process is generally much more rapid than the former, and hence it is only under the special conditions existing in electrolysis that appreciable amounts of dithionate are formed. It must be

TABLE 18

Comparison of gases obtained in electrolysis of acetate and by action of persulfate

| GASES | OBTAINED BY ACTION OF PERSULFATE | OBTAINED IN ELECTROLYSIS OF ACETATE |
|-------------------------------------|-------------------------------------|--|
| | <i>per cent</i> | <i>per cent</i> |
| CO ₂ | 80.2 | 82.6 |
| O ₂ | 0.1 | 0.3 |
| C ₂ H ₄ | 0.4 | 0.2 |
| CO..... | 0.6 | 0.5 |
| H ₂ | 0.2 | 0.1 |
| C ₂ H ₆ | 9.8 | 10.2 |
| CH ₄ | 8.6 | 5.2 |

remembered that the relatively dilute solution of hydrogen peroxide involved in chemical oxidation may behave quite differently, especially when two alternative reactions are possible, from the thin layer of hydrogen peroxide, of high concentration, which would be formed continuously at an anode.

It may be recorded in support of this view that persulfates, which hydrolyze gradually in solution to yield a continuous supply of hydrogen peroxide, can often imitate anodic processes even when hydrogen peroxide itself does not do so. As an illustration may be quoted the oxidation of acetates: the action of hydrogen peroxide, under various experimental conditions, was found to give mainly oxygen together with some carbon dioxide, but only very small amounts of ethane and methane. When persulfate is used as the oxidizing agent, however, appreciable quantities of ethane and methane can be obtained. In table 18 is given the analysis

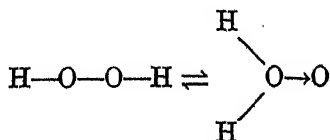
of the gas resulting from the action of 30 g. of 93 per cent sodium persulfate on a solution of 75 cc. of 0.1 *N* acetic acid and 0.1 *N* potassium acetate at 85°C.; the figures may be compared with those obtained by the electrolysis of a solution of 4 *N* acetic acid and 4 *N* potassium acetate with a platinum anode at a current density of 0.0025 ampere per square centimeter (20).

The oxidizing action of persulfate is thus similar to that of an anode at low current density. The presence of manganese and cobalt salts, which catalyze the decomposition of hydrogen peroxide, in the mixture of persulfate and acetate was found to inhibit the formation of hydrocarbons, as observed in the electrolytic oxidation of acetate. It is important to note, further, that when the catalysts were added the rate of gas evolution was decreased, although the gas often contained relatively large amounts of oxygen: this result implies that the behavior of the catalysts is not due to their action on persulfate, but on a substance formed from it, presumably hydrogen peroxide, which is the effective agent for the production of hydrocarbons by oxidation of the acetate.

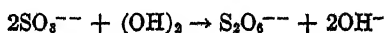
It has been shown in recent years by Fichter and his coworkers that many of the oxidations brought about electrolytically can be closely imitated using fluorine as oxidizing agent (11). The exact significance of this, however, seems to have been overlooked. Fichter formally represents the oxidations as involving change of electrical charge only, by the conversion of a fluorine atom to an ion; since the oxidations only take place in aqueous solution, however, and since fluorine reacts instantly with water, it does not seem probable that this is the mechanism. Nor does the formation of nascent oxygen, in view of the work of the authors, seem to afford any likelihood of explaining the oxidations. On the other hand, it has been shown (4, 12) that under appropriate conditions of stabilization, the action of fluorine on a solution of potassium hydroxide gives primarily hydrogen peroxide, and it appears probable that the peroxide is always formed, although it may decompose rapidly to give oxygen. In this case, the hydrogen peroxide will be formed continuously in a thin layer of high local concentration on the surface of each bubble of fluorine, in exact imitation of what probably occurs at an anode. Hence the close similarity between the action of fluorine and electrolytic oxidation might be expected. It is interesting to note that, as the result of a study of a large number of anodic oxidations, Fichter and J. Müller (13) were led to state that "Von allen chemischen Oxydationsmitteln kommt das Wasserstoffperoxyd in seiner Wirkung dem anodischen Sauerstoff am nächsten."

The difference in behavior between hydrogen peroxide formed at an anode and the ordinary chemical reagent may be accounted for in at least two ways, which must be regarded as largely speculative. In the first place, it was suggested by

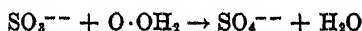
Raikov (35) that hydrogen peroxide is a tautomeric system comprising a dihydroxyl and peroxide form:



and Geib and Harteck (17) claim to have isolated II by the action of hydrogen atoms on oxygen at low temperatures. If Raikov's view is correct, it is possible that the unique reactions of hydrogen peroxide are due to I, and general oxidation, indistinguishable from that of active oxygen, to II; thus in the formation of dithionate we should have

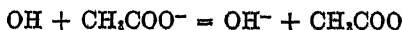


while in sulfate production



At the moment of the formation of hydrogen peroxide by the combination of discharged hydroxyl radicals, the dihydroxyl form is likely to predominate, and hence it is probable that the unique reactions of hydrogen peroxide will be more marked electrolytically than when the ordinary chemical reagent is employed. At high current densities the concentration of the dihydroxyl form relative to the peroxide form is likely to be raised, and hence we should expect that where two anodic oxidations are possible, the characteristic oxidation should be favored by high current density; this has already been shown to be the case.

Another possibility is that the active anodic oxidant is the hydroxyl radical; this would certainly account for the speed and vigor of the oxidation, but it would be necessary to make several subsidiary assumptions to account for the experimental facts. To explain the influence of anode material and catalysts for hydrogen peroxide decomposition in various electrolytic processes, it must be postulated that the catalytic decomposition of hydrogen peroxide occurs through the intermediate formation of hydroxyl radicals. The specific reactions of the peroxide, such as the conversion of sulfite to dithionate, would then be ascribed to these radicals. This point of view is fundamentally the same as that which attributes the oxidizing action to a form of hydrogen peroxide, except that it ascribes the characteristic behavior of the compound to an intermediate species whose chemical properties cannot be studied. Since hydrogen peroxide is known to be produced anodically, it seems preferable, for the present, to assume that this is the active oxidizing agent, especially as when it is formed at high concentration at the anode, perhaps in an active form as suggested above, its properties might be somewhat different from those of the ordinary reagent. A serious objection to the suggestion that hydroxyl radicals are responsible for anodic oxidation is the fact that in the Kolbe reaction the potential set up, presumably due to the discharge of acetate radicals, is much higher than that required for the discharge of hydroxyl ions and the evolution of oxygen; to account for this, it would be necessary to suppose that the process



is irreversible. Although this is possible, it does not appear to be very probable.

The theory of the anodic formation of hydrogen peroxide has been criticized adversely by Walker and Weiss (44) and by Butler and Leslie (8), chiefly on the grounds that (a) it is unlikely that hydroxyl radicals will combine together in solution to give hydrogen peroxide, and (b) the effect of catalysts can be explained in an alternative manner. With regard to the first criticism, there appears to be no reason to suppose that the process is impossible. It seems to be proved conclusively by the work of Rodebush and Wahl (39) and of Oldenberg (34) that hydroxyl radicals do actually combine in the gas phase to yield hydrogen peroxide, and there seems to be no fundamental objection to the postulate that the same process occurs in solution. If hydroxyl radicals do not unite to give hydrogen peroxide in solution, the observed formation of the peroxide with a glow-discharge anode must be accounted for, and certainly no satisfactory alternative explanation has yet been proposed. The second criticism is based to a large extent on the fact that the addition of certain metallic salts, e.g., lead, silver, and manganese, leads to the deposition of oxides on the anode with consequent lowering of the anode potential and inhibition of the electrolytic oxidation process. The authors have frequently noted that metallic oxides are formed on the anode, but this is not usually the case: for example, the presence of ferrous or ferric salts diminishes oxidation of those depolarizers in which direct reaction with hydrogen peroxide has been suggested, but no anodic deposit is formed. Such a deposit is, in fact, not expected, since the catalytic effect of ferrous and ferric ions is generally attributed to purely homogeneous reactions; on the other hand the activity of manganese, lead, and silver ions is probably due to the higher oxides, and anodic deposits of these oxides might be anticipated. That such deposits are not essential, however, is also proved by the fact that insoluble catalysts, particularly powdered charcoal, have been found to reduce the anodic efficiency in several instances. It is true, of course, that the effect of a catalyst is most marked when the active agent, e.g., higher oxide or ion, is produced at the anode where the hydrogen peroxide is formed. An extremely important aspect of this question is that the addition of catalysts for hydrogen peroxide decomposition frequently raises, not lowers, the potential to a marked extent, e.g., in the electrolysis of thio-sulfate or sulfite solutions, yet the oxidation is inhibited; facts of this kind are not easily explained without the assumption that the factors responsible for the anodic process and the potential are to a great extent independent.

The theoretical views of the present authors have been criticized by Bancroft⁸ (3), who puts forward the objection that hydrogen peroxide is only a moderately weak oxidizing agent with a potential of about 1.16

⁸ This paper contains a number of misstatements and misrepresentations, to which it is hoped to refer in greater detail elsewhere.

volts in acid solution (5); if hydrogen peroxide gave rise to a reversible oxidation-reduction system this objection would be valid, but it is very doubtful whether it does so, and whether the potential quoted has any fundamental significance. The fact that hydrogen peroxide is able to liberate chlorine from hydrochloric acid solution, the reversible potential for which is about 1.35 volts, shows that the situation is by no means as simple as has been supposed. Bancroft's statement, "If Glasstone and Hickling were right, the electrode of the lead storage cell would be an impossibility," is based on a failure to understand the hydrogen peroxide theory.

V. CONCLUSION

In concluding this review it can be stated definitely that no serious objection to the theory of the anodic formation of hydrogen peroxide has been put forward, and no alternative view has been proposed which is able to account in such a simple and complete manner for the observed phenomena of electrolytic oxidation. The authors would welcome any other view capable of explaining adequately the large variety of facts mentioned in this paper, but for the time being there is no doubt that the hydrogen peroxide theory provides a valuable guide for the interpretation of many anodic processes. When further investigations are made, it is hoped to develop the theory even further and widen its scope so as to include observations which are still difficult to understand.

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